

(4.55), 212.5 (4.72); calcd for $C_{19}H_{12}O_3$, parent ion m/e 288.079, found 288.080.

Spectral properties of 8-methoxy-7,12-benz[*a*]anthraquinone: NMR (FT-100 MHz) ($CDCl_3$) δ 9.59 (m 1 H), 8.31–7.27 (m 8 H), 4.06 (s, 3 H); IR ($CHCl_3$) 1665, 1590, 1470, 1450, 1275, 995 cm^{-1} ; UV (ethanol) λ ($\log \epsilon$) 386 (3.87), 282 (4.48), 231 (4.42), 211 (4.65); calcd for $C_{19}H_{12}O_3$, parent ion m/e 288.079, found 288.081.

Pr(fod)₃ Experiment. A solution of 114.7 mg of Pr(fod)₃ in 2 mL of $CDCl_3$ was added in small aliquots via syringe to prepared solutions of methoxybenz[*a*]anthraquinone (5–15-mg sample) in 0.5 mL of $CDCl_3$ in a NMR tube. The NMR spectra were recorded on a Varian XL-100 spectrometer in the FT mode. The shifts of the methoxy and C_1 -H were recorded after each addition of praseodymium solution. For these data and plots of the chemical shift of the C_1 -H vs. the sum of the shifts of the methoxy and C_1 -H,¹⁵ see the supplementary material in the microfilm edition.

Eu(fod)₃ Experiment. A solution of 188.1 mg of Eu(fod)₃ in 2 mL of $CDCl_3$ was added via syringe in small aliquots to a prepared solution of methoxybenz[*a*]anthraquinone (10–20-mg sample) in 0.5 mL of $CDCl_3$ in a NMR tube. After each addition of europium reagent, the NMR spectrum was recorded on a Varian XL-100 in the FT mode. The shifts of the methoxy and C_1 -H were recorded. For these data and a plot of the chemical shifts of the C_1 -H vs. the sum of the shifts of the C_1 -H and methoxy,¹⁵ see the supplementary material in the microfilm edition.

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Registry No.—Va, 65915-31-3; Vb, 65915-32-4; 8-OMe-VI, 65915-33-5; 11-OMe-VI, 65915-34-6; 1,4-phenanthraquinone, 569-15-3; 1-methoxy-1,3-cyclohexadiene, 2161-90-2.

Supplementary Material Available: observed proton shifts of 11-methoxy-7,12-benz[*a*]anthraquinone and 8-methoxy-7,12-benz[*a*]anthraquinone with Pr(fod)₃ (Tables I and II) and Eu(fod)₃ (Tables III and IV) and plots of the shift of C_1 -H vs. the sum of C_1 -H and OCH_3 with Pr(fod)₃ and Eu(fod)₃ (Figures I and II) (4 pages). Ordering information is given on any current masthead page.

References and Notes

- J. C. Arcos and M. F. Argus, "Chemical Induction of Cancer", Vol. IIA, Academic Press, New York, N.Y., 1974, pp 32, 54, 55, 67, 71–73, 165, 174–175, 186, and 336.
- P. O. P. Ts'o and J. A. DiPaolo, "Chemical Carcinogenesis", Part B, Marcel Dekker, New York, N.Y., 1974.
- L. F. Fieser and R. B. Sandin, *J. Am. Chem. Soc.*, **62**, 3098 (1940).
- M. S. Newman and V. Sankaran, *Tetrahedron Lett.*, 2067 (1977).
- B. I. Rosen and W. P. Weber, *J. Org. Chem.*, **42**, 3463 (1977).
- J. E. Tomaszewski, W. B. Manning, and G. M. Muschik, *Tetrahedron Lett.*, 971 (1977).
- R. G. Harvey, P. P. Fu. C. Cortez, and J. Pataki, *Tetrahedron Lett.*, 3533 (1977).
- W. B. Manning, J. E. Tomaszewski, G. M. Muschick, and R. I. Sato, *J. Org. Chem.*, **42**, 3465 (1977).
- T. R. Kelly, J. W. Gillard, R. N. Goerner, and J. M. Lyding, *J. Am. Chem. Soc.*, **99**, 5513 (1977).
- R. G. F. Gilles and G. H. P. Roos, *Tetrahedron Lett.*, 4159 (1975).
- P. M. Brown and R. H. Thomson, *J. Chem. Soc., Perkin Trans. 1*, 997 (1976).
- H. M. McConnel and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).
- National Cancer Institute Safety Standards for Research Involving Chemical Carcinogens. DHEW Publication No. (NIH) 76-900.
- A. J. Birch, E. M. A. Shookry, and F. Stansfield, *J. Chem. Soc.*, 5376 (1961).
- K. L. Servis and D. J. Bowler, *J. Am. Chem. Soc.*, **95**, 3393 (1973).

A One-Flask Preparation of Analytically Pure $K_2Fe(CO)_4$

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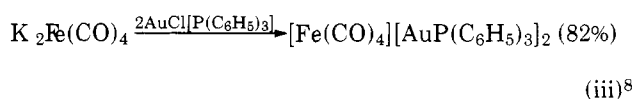
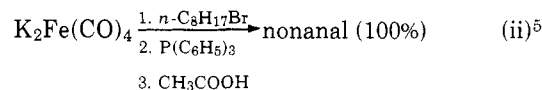
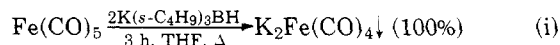
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The use of the highly nucleophilic tetracarbonylferrate dianion, $[Fe(CO)_4]^{2-}$, in organic and inorganic syntheses has

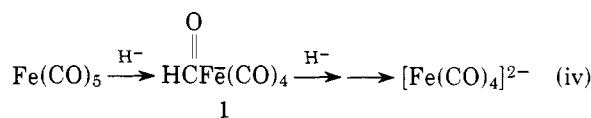
markedly grown in recent years. Numerous useful carbon-carbon bond-forming reactions can be effected with this reagent.¹ It also serves as a starting material for the preparation of a variety of iron carbonyl π complexes (cyclobutadiene, trimethylenemethane, *o*-xylylene) and mixed metal complexes such as $[(CH_3)_2SnFe(CO)_4]_2$ and $[HgFe(CO)_4]_n$.² Syntheses of $[Fe_2(CO)_8]^{2-}$ and polynuclear clusters such as $H_2Fe-Ru_2Os(CO)_{13}$ from $[Fe(CO)_4]^{2-}$ have recently been communicated.^{3,4}

We report in this note a novel and convenient one-flask synthesis of analytically pure $K_2Fe(CO)_4$. While $K_2Fe(CO)_4$ has not been used as extensively as $Na_2Fe(CO)_4$ or $Na_2Fe(CO)_4$ -dioxane, parallel reactivity has been observed for alkylation reactions,⁵ and some useful organic transformations employing $K_2Fe(CO)_4$ have been reported.⁶ Unlike $Na_2Fe(CO)_4$, $K_2Fe(CO)_4$ is not spontaneously flammable in air.

In typical procedures 1 equiv of $Fe(CO)_5$ was added to 2.1–2.5 equiv of commercially available $K(s-C_4H_9)_3BH^7$ at room temperature. After a 3–4 h reflux period, cooling afforded a 95–100% yield of analytically pure $K_2Fe(CO)_4$ as a white precipitate (eq i). After isolation by Schlenk or glove box techniques, additional reactions were carried out to provide chemical characterization (eq ii and iii).



Production of $K_2Fe(CO)_4$ proceeds via the rapidly formed and spectroscopically observable intermediate metal formyl 1 (eq iv). This compound was originally synthesized by Collman and Winter by formylation of $Na_2Fe(CO)_9$ with formic acetic anhydride. More recently, we¹⁰ and others^{11,12} have found that salts of 1 may be formed by attack of suitable hydride donors upon $Fe(CO)_5$. Conversion of 1 to $K_2Fe(CO)_4$ is the slow step. Since at no time are $Fe(CO)_5$ and $[Fe(CO)_4]^{2-}$ simultaneously present, the binuclear complex $[Fe_2(CO)_8]^{2-}$ is not formed.³ Other preparations of $[Fe(CO)_4]^{2-}$ require close monitoring to ensure this byproduct is not produced.⁵



For many years, $K_2Fe(CO)_4$ (of questionable purity) was available only by reaction of ethanolic or aqueous KOH with $Fe(CO)_5$.¹³ More recently, $K_2Fe(CO)_4$ has been synthesized from elemental potassium⁵ and its crystal structure has been determined.¹⁴ However, this procedure is experimentally more elaborate than ours, and a recrystallization is required to produce $K_2Fe(CO)_4$ of comparable purity. Since $K(s-C_4H_9)_3BH$ is considerably more expensive than potassium, the utility of our procedure is greatest with small to medium scale preparations where analytically pure product is desired. Attempts to synthesize $Li_2Fe(CO)_4$ or $Na_2Fe(CO)_4$ by reaction of $Fe(CO)_5$ with $Li(C_2H_5)_3BH$, $Li(s-C_4H_9)_3BH$, $Na(C_2H_5)_3BH$, or $Na(CH_3O)_3BH$ were unsuccessful. Although trialkyl borohydrides can be readily prepared from MH (M = Li, Na, K) and trialkylboranes,¹⁵ we have not found variations of our procedure employing a catalytic amount of $(C_2H_5)_3B$ or $(s-$

$C_4H_9)_3B$ and a stoichiometric amount of KH to be satisfactory.

This route to $K_2Fe(CO)_4$ extends previous work by us^{10,16} on the synthesis of transition metal monoanions by trialkyl borohydride cleavage of metal carbonyl dimers. Exploratory experiments indicate that trialkyl borohydrides are not sufficiently strong reductants to produce more highly reduced species such as metal carbonyl trianions.¹⁷ The conversion $1 \rightarrow K_2Fe(CO)_4$ poses an intriguing mechanistic question and is currently under investigation.

Experimental Section

General. All reactions were conducted under a N_2 atmosphere. THF was dried and deoxygenated by distillation from sodium benzophenone ketyl. Infrared spectra were obtained on a Perkin-Elmer Model 521 spectrometer, and elemental analyses were conducted by Gailbraith.

$K_2Fe(CO)_4$. To a dried 200-mL round-bottom flask was added 70 mL of 0.5 M $K(s-C_4H_9)_3BH$ (35 mmol)⁷ followed by 2.2 mL of $Fe(CO)_5$ (3.22 g, 16.5 mmol). The reaction mixture was refluxed for 4 h. After cooling, the resultant white solid was filtered (in a glove box or via Schlenk techniques) and washed with 50 mL of hexane. After vacuum drying, 4.0 g of analytically pure $K_2Fe(CO)_4$ (16.2 mmol, 98%, mp 270–273 °C dec) was obtained. Anal. Calcd: C, 19.85; Fe, 22.60. Found: C, 19.94; Fe, 22.38.

Caution: Since the byproduct ($s-C_4H_9)_3B$ is spontaneously flammable when pure, we recommend that the waste solvents be treated with an appropriate amount of a mild oxidizing agent (clorox, dilute H_2O_2) before disposal.

$Fe(CO)_4[AuP(C_6H_5)_3]_2$. To a 25-mL round-bottom flask containing a magnetic stirring bar were added 0.051 g of $K_2[Fe(CO)_4]$ (0.207 mmol), 0.2052 g of $(C_6H_5)_3PAuCl$ ¹⁸ (0.417 mmol), and 15 mL of THF. After being stirred for 12 h, the reaction mixture was gravity filtered. Methanol (15 mL) was added to the filtrate and the solution was concentrated to a cloud point on a rotary evaporator. Cooling to 0 °C for 12 h afforded brown-yellow crystals which were isolated by suction filtration, washed with methanol, and vacuum dried (0.1735 g). A second crop was obtained (0.0101 g) for a total yield of 0.184 g (0.169 mmol; 82% based upon $K_2[Fe(CO)_4]$) (IR (THF) 2002, 1929, 1893 cm^{-1} ; mp 145–150 °C dec).

Nonanal from Octyl Bromide. This procedure is similar to the $[Fe(CO)_4]^{2-}$ assay reported by Collman.⁵ To a 25-mL round-bottom flask was added 0.0945 g of $K_2[Fe(CO)_4]$ (0.0384 mmol), 0.08 mL of octyl bromide (0.463 mmol), and 0.1325 g of $(C_2H_5)_3P$ (0.508 mmol). The mixture was stirred for 12 h followed by addition of 200 μ L of glacial acetic acid and 100 μ L of tridecane. Gas chromatographic analysis (with reference to tridecane) indicated a 100% yield of nonanal based upon $K_2[Fe(CO)_4]$.

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Registry No.—Octyl bromide, 111-83-1; nonanal, 124-19-6; $K_2Fe(CO)_4$, 16182-63-1; $K(s-C_4H_9)_3BH$, 54575-49-4; $Fe(CO)_5$, 13463-40-6; $Fe(CO)_4[AuP(C_6H_5)_3]_2$, 16027-25-1; $(C_6H_5)_3PAuCl$, 14243-64-2.

References and Notes

- J. P. Collman, *Acc. Chem. Res.*, **8**, 342 (1975).
- J. E. Ellis, *J. Organomet. Chem.*, **86**, 1 (1975).
- J. P. Collman, R. K. Rothrock, R. G. Finke, and F. Rose-Munch, *J. Am. Chem. Soc.*, **99**, 7381 (1977).
- G. L. Geoffroy and W. L. Gladfelter, *J. Am. Chem. Soc.*, **99**, 7565 (1977).
- J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 2515 (1977).
- H. Masada, M. Mizuno, S. Suga, Y. Watanabe, and Y. Takegami, *Bull. Chem. Soc. Jpn.*, **43**, 3824 (1970), and preceding papers in this series.
- Sold by the Aldrich Chemical Co. as a 0.5 M THF solution under the trade name K-Selectride.
- C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1741 (1964).
- J. P. Collman and S. R. Winter, *J. Am. Chem. Soc.*, **95**, 4089 (1973).
- J. A. Gladysz, G. M. Williams, W. Tam, and D. L. Johnson, *J. Organomet. Chem.*, **140**, C1 (1977).
- C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, **98**, 5395 (1976).
- S. R. Winter, G. W. Cornett, and E. A. Thompson, *J. Organomet. Chem.*, **133**, 399 (1977).
- (a) P. Krumholz and H. M. A. Stettiner, *J. Am. Chem. Soc.*, **71**, 3035 (1949). See also (b) Y. Takegame, Y. Watanabe, T. Mitsudo, and H. Masada, *Bull. Chem. Soc. Jpn.*, **42**, 202 (1969).
- R. G. Teller, R. G. Finke, J. P. Collman, H. B. Chin, and R. Bau, *J. Am. Chem. Soc.*, **99**, 1104 (1977).
- C. A. Brown, *J. Am. Chem. Soc.*, **95**, 4100 (1973); H. C. Brown, A. Khuri, and S. C. Kim, *Inorg. Chem.*, **16**, 2229 (1977).
- See also (a) J. A. Gladysz, J. L. Hornby, and J. E. Garbe, *J. Org. Chem.*, **43**, 1204 (1978), and (b) J. A. Gladysz and W. Tam, *J. Am. Chem. Soc.*, **100**, 2545 (1978).
- J. E. Ellis and R. A. Faltynek, *J. Am. Chem. Soc.*, **99**, 1801 (1977); J. E. Ellis, P. T. Barger, and M. L. Winzenburg, *J. Chem. Soc., Chem. Commun.*, 686 (1977).
- B. J. Gregory and C. K. Ingold, *J. Chem. Soc. B*, 276 (1969).

Thallium in Organic Synthesis. 50. A Convenient Synthesis of Thallium(I) Cyanide, a Useful Reagent in Organic Synthesis^{1,2}

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Thallium(I) cyanide has previously been prepared either by precipitation from an aqueous solution of thallium(I) nitrate with potassium cyanide⁴ or by exchange between aqueous potassium cyanide and the thallium(I) form of Dowex-50 ion exchange resin.⁵ The first of these procedures requires repeated fractional recrystallization of the crude product and the use of CO_2 -free water (to avoid the formation of thallium(I) carbonate); the second procedure requires a large excess of the cation exchange resin. Both procedures are complicated by the formation of complexes with counterions (e.g., K^+). For these reasons, thallium(I) cyanide has received little attention as a reagent for organic synthesis.

We wish to describe a convenient and quantitative preparation of anhydrous thallium(I) cyanide under nonaqueous conditions by the reaction of dry hydrogen cyanide with thallium(I) phenoxide, together with some preliminary results on the utilization of this reagent for the preparation of α -ketonitriles, cyanofornates, and trimethylcyanosilane.

Use of Thallium(I) Cyanide in Synthesis. Stirring equimolar amounts of thallium(I) cyanide and an aroyl chloride in ether or ethyl acetate as solvent at room temperature for 1–3 hr, followed by removal of insoluble thallium(I) chloride and evaporation of the solvent, gives aromatic α -ketonitriles. This simple entry into these intriguing intermediates is to be contrasted with the classical method for their preparation which involves distilling aroyl chlorides over heavy-metal cyanides such as mercuric cyanide, cuprous cyanide, or silver cyanide, or addition of pyridine to a mixture of an aroyl chloride and hydrogen cyanide in ether,⁶ or by the utilization of phase transfer catalysis.⁷ In some instances, our procedure is unquestionably the method of choice. For example, *p*-nitrobenzoyl cyanide was obtained from *p*-nitrobenzoyl chloride and thallium(I) cyanide in 85% yield after 30 min at room temperature. By contrast, attempts to prepare this compound in satisfactory yield by previously available procedures have been reported to be singularly unsuccessful.⁸ Representative conversions of aroyl chlorides to aromatic α -ketonitriles are summarized in Table I.

The reaction is not generally applicable to aliphatic α -ketonitriles, since the initially formed products dimerize under the reaction conditions. Thus, reaction of thallium(I) cyanide with acetyl, propionyl, or pivaloyl chloride in ether at room