44, 43; UV (95% C_2H_5OH) λ_{max} 250 nm (ϵ 4.2 × 10^3).

Methyl 2-Carbomethoxy-4-ethoxy-5-oxohexanoate (8). To a solution of 23 mg (1 mmol) of sodium in 3 mL of methanol and 15 mL of ether was added dropwise 789 mg (6.0 mmol) of dimethyl malonate. This was followed by dropwise addition of 838 mg of a mixture of **3** and **4** (4.2 mmol of **3**). The solution was then refluxed for 24 h. After cooling, it was acidified with 1 N HCl, washed twice with 10 mL of water, once with saturated aqueous $NaHCO_3$, and again with water. After drying ($MgSO_4$) and concentration in vacuo 1.12 g of a crude product was obtained. This crude product was found by GLC analysis using tetradecane as an internal standard to contain 620 mg of **8** (59% yield). Preparative GLC (Column B) was used to further purify **8:** IR 1750, 1735, 1715 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 2.20 (s, ≈3 H), 2.1–2.4 (m, ≈2 H), 3.2–3.7 (m, 3 H), 3.77 (s, 6 H); mass spectrum (70 eV) *m/e* 203, 187, 143 (base), 115. Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.37; H, 7.34.

Dimethyl 2-Carbomethoxy-4-methoxyglutarate (9). When 1.311 g (11 mole) of **2**,[3] 1.744 g (13 mmol) of dimethyl malonate, and 2.1 mmol of sodium methoxide in an ether–methanol solution were refluxed for 4 days and the product isolated as above, the yield of **9** was estimated by GLC (column A) to be 58%. The crude product was subjected to bulb-to-bulb distillation followed by preparative GLC. **9:** IR 1745 (very broad) cm^{-1}; NMR ($CDCl_3$) δ 2.47 (m, 2 H), 3.47 (s, 3 H), 3.68 (s, 3 H), 3.74 (s, 6 H), 3.7 (m, ≈2 H); mass spectrum (70 eV) *m/e* 217, 189, 130 (base). Anal. Calcd for $C_{10}H_{16}O_7$: C, 48.39; H, 6.50. Found: C, 48.60; H, 6.32.

3-Ethoxy-2-pentanone (12). To a solution of lithium dimethylcuprate, prepared from 1.457 g (7.6 mmol) of cuprous iodide and 9 mL of 1.6 M methyllithium at 0 °C, was added a solution containing 2.75 mmol of **3** in 2 mL of ether. The mixture was stirred at room temperature for 3 h after which time it was diluted with 50 mL of ether and washed with dilute ammonium hydroxide until the aqueous layer was colorless. The ether layer was dried (Na_2SO_4) and concentrated by distillation. One half of the crude material was subjected to preparative GLC (column B) from which was obtained **12:** IR 2980, 1717 cm^{-1}; NMR ($CDCl_3$) δ 0.93 (t, J = 7 Hz, 3 H), 1.23 (t, J = 7 Hz, 3 H), 1.67 (q, J = 7 Hz, 2 H), 2.13 (s, 3 H), 3.47 (q, J = 7 Hz, ≈2 H), 3.57 (t, J = 7 Hz, ≈1 H).

From the other half of the crude material was obtained 204 mg of a semicarbazone: mp 109–11 °C (lit.[23] mp 93–5 °C); NMR ($CDCl_3$) δ 0.90 (t, J = 7 Hz, 3 H), 1.2 (t, J = 7 Hz, 3 h), 1.5 (m, ≈2 H), 1.83 (s, ≈3 H), 3.37 (q, J = 7 Hz, 2 H), 3.67 (t, J = 7 H_z, 1 H), 5.83 (broad s, 2 H). Anal. Calcd for $C_8H_{17}O_2N_3$: C, 51.32; H, 9.15; N, 22.44. Found: C, 51.29; H, 8.90; N, 22.34.

***endo*- and *exo*-2-Carbomethoxy-2-methoxy-5-norbornene (17a and 17b).** A stainless steel bomb containing 1.005 g (8.7 mmol) of **2** and 5.04 g (77 mmol) of cyclopentadiene was heated at 165 °C for 12 h. The reaction mixture was chromatographed on silica gel. The portion eluting with chloroform yielded 850 mg of **17** (53% yield). The endo and exo isomers were separated by preparative GLC (column C). The reaction mixtures before column chromatography had been found by GLC to contain a 38:62 ratio of the isomers. They were identified as below.

Shorter retention time isomer (**17a**): IR 2950, 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.5–2.1 (m, 4 H), 2.9 (m, ≈1 H), 3.1 (m, ≈1 H), 3.23 (s, 3 H), 3.71 (s, 3 H), 5.88 (d of d, J_1 = 3 Hz, J_2 = 6 Hz, 1 H), 6.28 (d of d, J_1 = 3 Hz, J_2 = 6 Hz, 1 H); mass spectrum (70 eV) *m/e* 182 (P), 117 (base). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.93; H, 7.68.

Longer retention time isomer (**17b**): IR 2950, 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.2–1.8 (m, 3 H), 2.27 (d of d, J_1 = 3 Hz, J_2 = 12 Hz, 1 H), 2.9 (m, 1 H), 3.13 (s, 3 H), 3.3 (m, 1 *H*), 3.80 (s, 3 H), 6.07 (d of d, J_1 = 3 Hz, J_2 = 6 Hz, 1 H), 6.40 (d of d, J_1 = 3 H_2, J_2 = 6 Hz, 1 H); mass spectrum (70 eV) *m/e* 182 (P), 117 (base).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 66.01; H, 7.73.

2-Ethoxy-2-acetyl-5-norbornene (18). In a stainless-steel bomb were placed 0.64 g of a mixture of **3** and **4** (4.2 mmol of **3**) and 3.7 g (55 mmol) of freshly distilled cyclopentadiene. The sealed bomb was kept in a sand bath at 160 °C for 40 h. Silica gel column chromatography of the reaction products afforded 464 mg (61% yield) of the Diels–Alder adduct, **18**, upon elution with benzene–chloroform (1:1). Preparative GLC (column C) afforded an analytical sample of the mixture of endo and exo isomers of **18:** IR 3050, 2970, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.17 (t, J = 7 Hz, *endo*-OCH_2CH_3), 1.22 (t, J = 7 Hz, *exo*-$O\text{-}CH_2CH_3$), 1.3–2.0 (m, 4 H), 2.20 (s, *endo*-$COCH_3$), 2.30 (s, *exo*-$COCH_3$), 2.7–3.4 (m, 4 H), 5.8–6.4 (m, 2 H).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.42; H, 8.84.

4-Carbomethoxy-4-methoxycyclohexene (19). A sealed bomb containing 2.03 g (17.4 mmol) of **2**, approximately 5 g (90 mmol) of butadiene, and 10 mg of hydroquinone was heated at 190 °C for 56 h. The reaction mixture was extracted with 100 mL of hot acetonitrile and the residue from the concentration of that solution was chromatographed on a silica gel column. The fraction eluted with benzene–chloroform (1:1) contained 1.45 g of **19** (49% yield). This material was further purified by bulb-to-bulb distillation. **19:** IR 1735, 1655 cm^{-1} NMR ($CDCl_3$) δ 2.0 (m, 4 H), 2.4 (m, 2 H), 3.24 (s, 3 H), 3.74 (s, 3 H), 5.64 (bs, 2 H); mass spectrum (70 eV) *m/e* 139, 112 (base). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.56; H, 8.40.

4-Ethoxy-4-acetylcyclohexene (20). A solution of 978 mg of a mixture of **3** and **4** (4.3 mmol of **3**), 4 g (74 mmol) of butadiene, and 10 mg of hydroquinone in 5 mL of benzene was placed in a stainless-steel bomb and heated at 190 °C for 70 h. The reaction mixture was treated as above to give 290 mg (40% yield) of **20.** A bulb-to-bulb distillation afforded a sample of **20** for analysis: IR 3030, 1710, 1652 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 1.7–2.4 (m, 6 H), 2.20 (s, 3 H), 3.30 (q, J = 7 Hz, 2 H), 5.65 (br s, 2 H); mass spectrum (70 eV) *m/e* 125, 97, 80. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.54; H, 9.73.

Registry No.—**2,** 7001-18-5; **3,** 65915-73-3; **4,** 51933-13-2; **8,** 65915-74-4; **9,** 65942-40-7; **12,** 65915-75-5; **12** semicarbazone, 65915-76-6; **17a,** 65915-77-7; **17b,** 65915-78-8; *exo*-**18,** 65915-79-9; *endo*-**18,** 65915-80-2; **19,** 65915-81-3; **20,** 65915-82-4; dimethyl malonate, 108-59-8; cyclopentadiene, 542-92-7; butadiene, 106-99-0.

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(23) The difference in melting point between our semicarbazone (109–11 °C) and that reported in the literature (93–5 °C)[24] may be due to geometric isomerization of the semicarbazone. Indeed in one preparation, the crude semicarbazone had a melting range of 93–6 °C which changed to 103–8 °C after one recrystallization from water.
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Synthesis of 8-Methoxy- and 11-Methoxybenz[*a*]anthraquinones via Diels–Alder Reaction of 1,4-Phenanthraquinone

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We have been interested in the synthesis of oxygenated derivatives of 7,12-dimethylbenz[*a*]anthracene (one of the most potent carcinogenic polycyclic aromatic hydrocarbons).[1,2] Since excellent methods[3,4] exist to convert 7,12-

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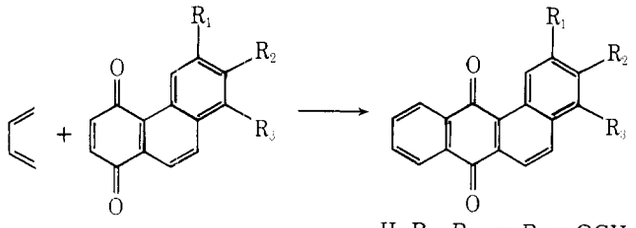
Scheme I



I, R_1, R_2, or R_3 = OCH_3 II, R_1, R_2, or R_3 = OCH_3

benz[*a*]anthraquinones into the corresponding 7,12-dimethylbenz[*a*]anthracene derivatives, synthesis of the former constitutes a solution to the problem.

Diels–Alder cycloadditions have been applied to the synthesis of related polycyclic aromatic compounds.[5–8] Thus, 2,3- and 4-methoxy-7,12-benz[*a*]anthraquinones may be prepared by a Diels–Alder reaction between 1,3-butadiene and 6-, 7-, or 8-methoxy-1,4-phenanthraquinone.[5] See Scheme I.

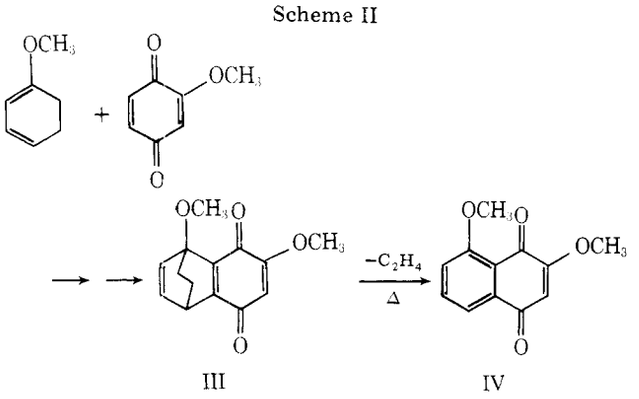
When reaction was attempted between 1-methoxy-1,3-butadiene and 1,4-phenanthraquinone, methanol was lost and only 7,12-benz[*a*]anthraquinone was isolated, even at low temperatures. Therefore, an alternative route was sought for the synthesis of the 8- and 11-methoxy-7,12-benz[*a*]anthraquinones.

Aromatic methoxy substituted compounds have been prepared via a Diels–Alder reaction[9,10] between a 1-methoxy-1,3-cyclohexadiene and 1,4-benzoquinone which gave an ethylene-bridged bicyclic intermediate, III, Scheme II. On pyrolysis, ethylene is eliminated in a retro-Diels–Alder reaction to give the aromatic methoxy compound IV.

In a similar fashion we reacted 1-methoxy-1,3-cyclohexadiene with 1,4-phenanthraquinone, Scheme III, to give in 75% yield two bridged bicycloadducts Va and Vb in a ratio of 18:82, as determined by NMR. The mixture of isomers was not separable on either silica or alumina thin layer chromatograms using a variety of solvent systems. After pyrolytic elimination of ethylene from the mixture, two products were isolated in quantitative yield. The isomers were separated by column chromatography in a ratio of 16:84, the more polar isomer predominating. They were identified by spectroscopic techniques (IR, NMR, UV, and high resolution mass spectrometry) and shown to be 8- and 11-methoxy-7,12-benz[*a*]anthraquinone (8-OMe-VI and 11-OMe-VI).

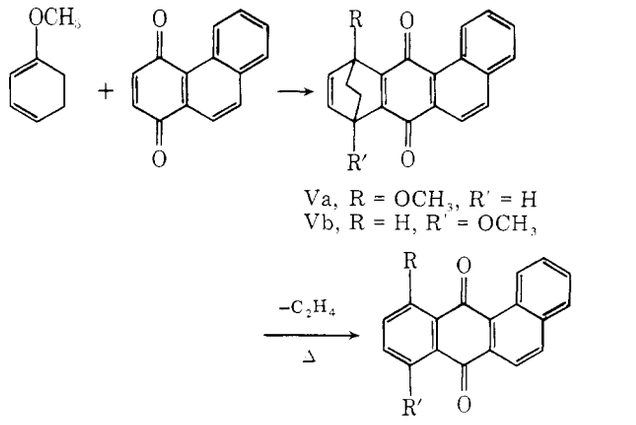
On the basis of steric interactions in transition state during the Diels–Alder reaction, one might expect that the 8-methoxy isomer (8-OMe-VI) would be predominant. In order to verify the structures of each isomer, experiments were done using lanthanide shift reagents, $Eu(fod)_3$ and $Pr(fod)_3$. It is expected that the shift reagent will chelate to the quinone carbonyl possessing an adjacent methoxy ether functionality and one would observe the most rapid shift for the methoxy methyl group in both isomers. The chemical shift of C_1–H in 7,12-benz[*a*]anthraquinones is unique at δ 9.7.[11] In the 11-methoxy isomer, the shift of the C_1–H should be more rapid than the shift of C_1–H in the 8-methoxy isomer where it is located considerably further from the coordinated shift reagent. This is indeed observed. The McConnel–Robertson equation for pseudocontact shifts in lanthanide-substrate interactions predicts that when the internuclear angle between the carbonyl–Eu–H falls between 55 and 125°, an upfield shift will be observed.[12] Consistent with this prediction, the C_1–H of 11-methoxy-7,12-benz[*a*]anthraquinone experiences a significant upfield shift on addition of $Eu(fod)_3$, whereas the C_1–H of 8-methoxy-7,12-benz[*a*]anthraquinone does not. Please see supplementary material for supporting data.

Scheme II



III IV

Scheme III



Va, R = OCH_3, R′ = H
Vb, R = H, R′ = OCH_3

11-OMe-VI, R = OCH_3, R′ = H
8-OMe-VI, R = H, R′ = OCH_3

Experimental Section

The National Cancer Institutes safety standards for research involving chemical carcinogens were followed.[13] IR spectra were determined in chloroform solution using matched 0.01-mm NaCl cells on a Perkin-Elmer 281 spectrometer and were calibrated against known bands in polystyrene. Ultraviolect spectra were obtained in 95% ethanol on a Beckman Acta M spectrometer. NMR spectra were determined on a Varian XL-100 instrument in the FT mode. Melting points were taken on a Hoover–Thomas apparatus and are uncorrected. High-resolution mass spectra were run at the California Institute of Technology Microanalytical Laboratory, Pasadena, Calif. on a duPont 21-492 mass spectrometer.

Preparation of Va and Vb. A solution of benzene (65 mL), 1,4-phenanthraquinone[5] (278.4 mg; 1.338 mmol), and 1-methoxy-1,3-cyclohexadiene[14] (1.367 g; 12.42 mmol) was heated overnight at 94 °C in a pressure bottle. After cooling, the solvent was evaporated and the residue was chromatographed on a column, 2.5 × 17 cm, packed with 51 g of Alumina (MCB, 80–325 mesh, activated) eluting initially with hexane to remove excess diene and possible polymeric products of the diene. The column was next eluted with 10% ethyl acetate/hexane to remove traces of unreacted 1,4-phenanthraquinone. The final eluting solvent was 30% ethyl acetate/hexane. The desired adducts were obtained as an orange solid, 298.9 mg (0.946 mmol, 75% yield). The product was identified as a mixture of Va and Vb from its NMR spectra and from further chemical studies: NMR (100 MHz) ($CDCl_3$) δ 9.5 (m, 1 H), 8.2–7.5 (m, 5 H), 6.7–6.3 (m, 2 H), 4.56 (m, 1 H), 3.75 (s, 3 H), 2.9–2.4 (m, 4 H).

Preparation of 8-OMe-VI and 11-OMe-VI. The isomeric mixture of Va and Vb (80.6 mg; 0.253 mmol) was sublimed at 150 °C (0.15 mm) over 2 h in a vacuum sublimator. Isolated from the cold finger was 73.6 mg (0.253 mmol, 100% yield) of a mixture of 8- and 11-methoxy-7,12-benzanthraquinone. The isomers were separated on a 2.5 × 45 cm column packed with 81 g of silica (TLC grade Silica H, E. Merck Co.) eluting with 50% ethyl acetate/hexane with 80 psi pressure across the column. Recovered after chromatography were 10.8 mg of the less polar 11-methoxy-7,12-benzanthraquinone (mp 195 °C) and 61.4 mg of 8-methoxy-7,12-benzanthraquinone (mp 184–185 °C).

Spectral properties of 11-methoxy-7,12-benz[*a*]anthraquinone: NMR (FT-100 MHz) ($CDCl_3$) δ 9.38 (m, 1 H), 8.33–7.30 (m 8 H), 4.08 (s, 3 H); IR ($CHCl_3$) 1670, 1595, 1465, 1450, 1330, 1310, 1280, 1240–10, 1075, 995, 855 cm^{-1}; UV (ethanol) λ (log ϵ) 390 (3.84), 285 (4.58), 233

(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 ε) 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*]anthraquinones (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.

Acknowledgments. This investigation was supported by Grant No. 1R01-CA-19444-02 awarded by the National Cancer Institute, Department of Health, Education, and Welfare.

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_1H 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.

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

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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 $H_2FeRu_2Os(CO)_{13}$ 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).

$$Fe(CO)_5 \xrightarrow[3\text{ h, THF, }\Delta]{2K(s\text{-}C_4H_9)_3BH} K_2Fe(CO)_4\downarrow\ (100\%) \qquad \text{(i)}$$

$$K_2Fe(CO)_4 \xrightarrow[2.\ P(C_6H_5)_3]{1.\ n\text{-}C_8H_{17}Br} \underset{3.\ CH_3COOH}{\text{nonanal}}\ (100\%) \qquad \text{(ii)}^5$$

$$K_2Fe(CO)_4 \xrightarrow{2AuCl[P(C_6H_5)_3]} [Fe(CO)_4][AuP(C_6H_5)_3]_2\ (82\%) \qquad \text{(iii)}^8$$

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 $Na_2Fe(CO)_4$[9] with formic acetic anhydride. More recently, we[10] 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]

$$Fe(CO)_5 \xrightarrow{H^-} \underset{\mathbf{1}}{HC(O)Fe(CO)_4} \xrightarrow{H^-} [Fe(CO)_4]^{2-} \qquad \text{(iv)}$$

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 potassium[5] 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 exploying a catalytic amount of $(C_2H_5)_3B$ or (*s*-

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