$C_4H_9)_3B$ 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 → $K_2Fe(CO)_4$ 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 $K(s\text{-}C_4H_9)_3BH$ (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 $(s\text{-}C_4H_9)_3B$ 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 μL of glacial acetic acid and 100 μL 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; $K(s\text{-}C_4H_9)_3BH$, 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.

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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 cyanide[4] 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, cyanoformates, 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*-nitrobenzoylcyanide 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

Table I. Aromatic and Aliphatic α-Ketonitriles, RCOCN

R	Registry no.	Time, h	Temp, °C	Yield,[a] %	IR absorption, cm^{-1} CO	CN	Mp or bp, °C (mm) Obsd	Lit.	Ref
C_6H_5	613-90-1	1	23	74	1690	2230	30–32	32–33	10
m-$CH_3C_6H_4$	5955-74-8	1.5	31	89	1700	2245	130–133 (40)	133 (40)	*b*
p-$CH_3C_6H_4$	14271-73-9	12	23	78	1670	2220	45–46[d]	49–49.5	*c*
p-$CH_3OC_6H_4$	14271-83-1	2	23	45	1675	2210	59.1	58–59	*b*
o-ClC_6H_4	35022-42-5	1.5	31	81	1675	2230	34–36	35	*e*
m-$NO_2C_6H_4$	61017-48-9	2	23	74	1700	2225	33–34	33–34	*f*
p-$NO_2C_6H_4$	6048-20-0	0.5	23	85	1700	2250	111[h]	116	*g*
2-Furyl	6047-91-2	3	31	84	1665	2245	25	25	*i*
2-Thienyl	6007-78-9	3	23	50	1645	2215	52.5	51.5	*j*
Cyclopropyl	6047-92-3	1	23	49	1700	2210	40–42 (11)	45–55 (12)	*k*
$(CH_3)_3C$	42867-40-3	1.5	23[l]	45	1720	2210	117–120 (760)	120	*m*

[a] Isolated yields determined on recrystallized or distilled material. [b] F. Asinger, A. Saus, H. Offermanns, and H.-D. Hahn, *Justus Liebigs Ann. Chem.*, **691**, 92 (1966). [c] R. L. Soulen, S. C. Carlson, and F. Lang, *J. Org. Chem.*, **38**, 479 (1973). [d] C_9H_7NO requires: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.57; H, 4.85; N, 9.46. [e] *Beilstein*, Band X, 662 (1927). [f] L. Claisen and C. M. Thompson, *Chem. Ber.*, **12**, 1942 (1879). [g] A. Dornow and H. Grabhofer, *Chem. Ber.*, **91**, 1824 (1958). [h] $C_8H_4N_2O_3$ requires: C, 54.55; H, 2.29; N, 15.80. Found: C, 54.67; H, 2.55; N, 14.90. [i] E. Fischer and F. Brauns, *Chem. Ber.*, **46**, 892 (1913). [j] W. Steinkopf, *Justus Liebigs Ann. Chem.*, **540**, 14 (1939). [k] E. Zbiral and L. Fenz, *Monatsh. Chem.*, **96**, 1983 (1965). [l] Reaction run in *o*-dichlorobenzene. [m] B. A. Clement and R. L. Soulen, *J. Org. Chem.*, **39**, 97 (1974).

Table II. Aliphatic α-Ketonitrile Dimers, $(RCOCN)_2$

R	Registry no.	Time, h	Temp, °C	Yield,[a] %	IR absorption, cm^{-1} CO	CN	Mp, °C
CH_3	65378-56-5	1	23	75	1760	2270	69–70[b]
C_2H_5	65378-57-6	0.5	23	48[c]	1775	2250	58
$(CH_3)_3C$	65378-58-7	1	23	60[d]	1765	2225	54.8

[a] Isolated yields determined on recrystallized material. [b] Lit. mp 69.4–70.2 °C (B. E. Tate and P. D. Bartlett, *J. Am. Chem. Soc.*, **78**, 5575 (1956)). [c] $C_8H_{10}N_2O_2$ requires: C, 57.82; H, 6.07; N, 16.85. Found: C, 57.62; H, 5.91; N, 16.82. [d] $C_{12}H_{18}N_2O_2$ requires: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.67; H, 7.93; N, 12.41.

Table III. Cyanoformates, NCCOOR

R	Registry no.	Time, h	Temp, °C	Yield,[a] %	IR absorption, cm^{-1} CO	CN	Bp, °C (mm) Obsd	Lit.[b]
CH_3	17640-15-2	7[c]	35	66	1755	2250	95–97 (760)	95–96 (760)
C_2H_5	623-49-4	1	76	91	1750	2250	110–112 (760)	115–116 (760)
$(CH_3)_2CHCH_2$	59873-30-2	1	76	87	1750	2250	75–76 (80)	52–53 (20)

[a] Isolated yields determined on redistilled material. [b] Reference 9. [c] Reaction run in diethyl ether.

temperature gave only the corresponding α-ketonitrile dimers. We did prepare pivaloyl cyanide in 45% yield utilizing *o*-dichlorobenzene as solvent, but attempts to extrapolate this result to other aliphatic acid chlorides failed. This simple procedure represents a convenient route to these aliphatic α-ketonitrile dimers, many of which have not been reported previously (see Table II).

Reaction of alkyl chloroformates with thallium(I) cyanide in refluxing ethyl acetate gives alkyl cyanoformates (see Table III); reaction with potassium cyanide in the presence of 18-crown-6 is much slower.[9]

Trimethylcyanosilane[10a,b] is easily prepared (84% yield) by heating a mixture of trimethylchlorosilane and thallium(I) cyanide for 10 h without solvent.

We are currently exploring further synthetic applications of anhydrous thallium(I) cyanide.

Experimental Section

Thallium(I) Cyanide. Dry hydrogen cyanide, generated in situ from sodium cyanide and sulfuric acid, was bubbled for a few minutes through a stirred suspension of 6.0 g of thallium(I) phenoxide in 200 mL of refluxing dry ether (35 °C). The heavy white precipitate which rapidly formed was collected by filtration, washed with ether, and dried to give 4.6 g (100%) of thallium(I) cyanide, IR ν 2048 cm^{-1} (lit.[5] 2048 cm^{-1}).

General Method for the Preparation of Aromatic α-Ketonitriles. A suspension of 5.0 g (0.022 mol) of thallium(I) cyanide in 50 mL of dry ether or ethyl acetate was stirred vigorously under the conditions specified in Table I. The appropriate aroyl chloride (0.020 mol) was then added, and stirring was continued for the indicated period of time. The insoluble thallium(I) chloride which had precipitated was removed by filtration through Celite, the filtrate was evaporated under reduced pressure to remove solvent, and the crude product was purified either by fractional distillation or by recrystallization (see Table I). The method for the preparation of aliphatic α-ketonitrile dimers is the same as described above; conditions are specified in Table II.

General Method for the Preparation of Alkyl Cyanoformates. To a refluxing mixture of 5 g (0.022 mol) of thallium(I) cyanide in 50 mL of dry ethyl acetate was added 0.020 mol of the alkyl chloroformate, and the mixture was heated under reflux for the period of time indicated in Table III. When reaction was complete (as indicated by the disappearance of the characteristic absorption band at 1770 cm^{-1}), the reaction mixture was cooled to room temperature and filtered through Celite to remove precipitated thallium(I) chloride. Solvent was removed under reduced pressure and the product was purified by distillation (see Table III).

Trimethylcyanosilane. A suspension of 4.7 g (0.020 mol) of thallium(I) cyanide in 13 g (0.12 mol) of freshly distilled trimethylchlorosilane was heated under reflux overnight, and the precipitated thallium(I) chloride was removed by filtration through Celite. Excess trimethylchlorosilane was removed by distillation, and the product was distilled at 115–117 °, yield 1.66 g (84%). The product was identified by comparison with an authentic sample.

Registry No.—RCOCl (R = C_6H_5), 98-88-4; RCOCl (R = *m*-$CH_3C_6H_4$), 1711-06-4; RCOCl (R = *p*-$CH_3C_6H_4$), 874-60-2; RCOCl

(R = p-$CH_3OC_6H_4$), 100-07-2; RCOCl (R = o-ClC_6H_4), 609-65-4; RCOCl (R = m-$NO_2C_6H_4$), 121-90-4; RCOCl (R = o-$NO_2C_6H_4$), 122-04-3; RCOCl (R = 2-furyl), 527-69-5; RCOCl (R = 2-thienyl), 5271-67-0; RCOCl (R = cyclopropyl), 4023-34-1; RCOCl (R = $(CH_3)_3C$), 3282-30-2; RCOCl (R = CH_3), 75-36-5; RCOCl (R = C_2H_5), 79-03-8; ClCOOR (R = CH_3), 79-22-1; ClCOOR (R = C_2H_5), 541-41-3; ClCOOR (R = $(CH_3)_2CHCH_2$), 543-27-1; hydrogen cyanide, 74-90-8; thallium, 7440-28-0; thallium(I) cyanide, 13453-34-4; trimethylcyanosilane, 7677-24-9; trimethylchlorosilane, 75-77-4.

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Total Synthesis of *Racemic* α-Santalene and of *Racemic* Teresantalic Acid[1a]

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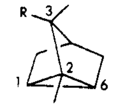
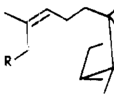
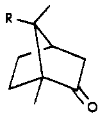
Representative examples of the tricyclene family of terpenes, characterized structurally by the presence of a 3,3-disubstituted 2-methylbicyclo[2.2.1.$0^{2,6}$]heptane skeleton, include the parent monoterpene tricyclene (**1a**) and its C-3 derivatives teresantalol (**1b**) and teresantalic acid (**1c**), as well as the sesquiterpenes α-santalene (**2a**) and α-santalol (**2b**).[2,3]



1a R = CH_3
b R = CH_2OH
c R = COOH



2a R = H
b R = OH

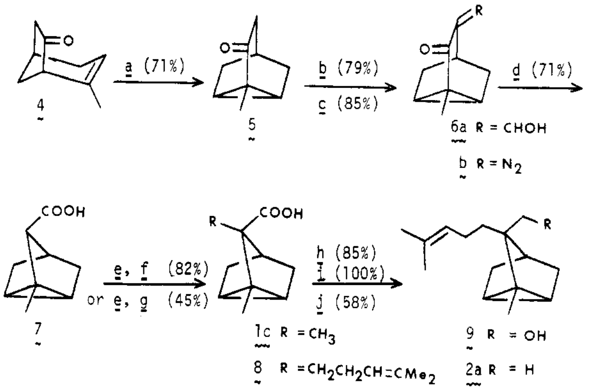


3a R = CH_2Br
b R = $CH_2CH_2CH_2Cl$

Although devoid of relative stereochemical relationships due to symmetry, these tricyclic carbon skeletons have attracted considerable synthetic interest. These efforts[4] have involved initial preparation of 7,7-disubstituted bicyclo[2.2.1]heptanones such as π-bromocamphor (**3a**)[4a] or chloro ketone **3b**[4b], cyclopropane ring closure via a carbene or carbenoid intermediate to generate the tricyclic skeleton, and subsequent functional group modification to yield the desired mono- and sesquiterpenes. We wish to report an alternative route to this general class of natural products which, via the intermediacy of tricyclic acid **7**, allows selective synthetic manipulation of *both* C-3 substituents of the tricyclene nucleus. This approach is illustrated by the total synthesis of *racemic* α-santalene (**2a**) and of *racemic* teresantalic acid (**1c**).

As shown in Scheme I, irradiation of the β,γ-unsaturated ketone **4**[5] in acetone resulted in a smooth rearrangement[6] to give the tricyclic α-methyl cyclopropyl ketone **5**. Conversion of **5** into the α′-formyl derivative **6a**, followed by treatment with tosyl azide yielded the diazo ketone **6b**,[7] which upon photolysis underwent ring contraction[8] to furnish the key intermediate, tricyclic acid **7**. Satisfactory generation of the dianion of acid **7** was achieved by exposure of **7** to lithium diisopropylamide (2.5 equiv, 50 °C)[9] *followed by* addition of n-butyllithium (1 equiv, 50 °C).[10,11] Alkylation of this dianion with methyl iodide yielded racemic teresantalic acid (**1c**). Alternatively treatment of the dianion with 5-iodo-2-methyl-2-pentene gave the 3,3-disubstituted acid **8**, which upon lithium aluminum hydride reduction yielded alcohol **9**, a structural isomer of the important natural product α-santalol (**2b**). Tosylation of alcohol **9** and reduction with lithium triethylborohydride furnished *racemic* α-santalene (**2a**).

Scheme I



[a] $h\nu$, acetone, 25 °C, 10 h. [b] NaH, ethyl formate, $Et_2O/EtOH$, 25 °C, 42 h. [c] Tosyl azide, Et_3N, CH_2Cl_2, 25 °C, 78 h. [d] $h\nu$, $NaHCO_3$, THF/H_2O, 25 °C, 45 min. [e] Lithium diisopropylamide (2.5 equiv), THF, 50 °C, 1 h; then n-BuLi (1 equiv) 50 °C, 1 h. [f] CH_3I, 25 °C, 16 h. [g] $Me_2C{=}CHCH_2CH_2I$, 25 °C, 20 h. [h] Lithium aluminum hydride, THF, reflux, 22 h. [i] Tosyl chloride, pyridine, 5 °C, 32 h. [j] Lithium triethylborohydride, THF, 25 °C, 72 h.

Experimental Section

General. All reactions were carried out in an inert nitrogen atmosphere and were routinely monitored by TLC or VPC using a Varian Aerograph 1200 instrument equipped with 5% SE-30 on Gas Chromosorb Q (100/120 mesh) ⅛ in. × 10 ft or 15% FFAP on Gas Chromosorb Q (100/120 mesh) ⅛ in. × 7 ft columns. Photochemical reactions were performed using a Hanovia 450 W, 3.7 A quartz high pressure mercury vapor lamp in a circulating ice-water cooled double-walled quartz immersion well. Photochemical solutions were deoxygenated by purging with dry nitrogen for 30 min and maintained at ca. 10 °C during irradiation. Melting points were determined on a Mel-temp apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 237B grading infrared spectrometer; ^{1}H-NMR spectra were measured on a Perkin-Elmer R-12 spectrometer, a Varian A-60 instrument equipped with cross correlation, or a Varian HA-100 instrument and chemical shifts are reported in ppm downfield (δ) from internal Me_4Si. ^{13}C-NMR spectra were obtained on a Bruker WH90 instrument and chemical shifts are reported in ppm downfield (δ) from internal Me_4Si. High-resolution mass spectra were obtained using a CEC Model 21-100 mass spectrometer. The microanalytical determination was done by Chemalytics, Inc., Tempe, Ariz.

2-Methyltricyclo[3.2.1.$0^{2,7}$]octan-3-one (5). Irradiation of 4-methylbicyclo[3.2.1]oct-3-en-6-one (3.91 g, 28.7 mmol) in acetone (300 mL) for 10 h resulted in complete disappearance of starting material. After evaporation of the acetone at reduced pressure, the dark residue was dissolved in Et_2O and filtered through aluminum oxide (30 g, activity III) and after evaporation of the solvent distilled to give 2.80 g (71%) of tricyclic ketone **5**: bp 45–47 °C (0.1 mm); IR (CCl_4) 3025 and 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 3), 1.1–1.5 (m, 1), 1.5–2.0 (m, 4), 1.94–2.08 (br d, 2, J = 4 Hz), 2.0–2.6 (m, 2); ^{13}C NMR ($CDCl_3$) 209.8 (s), 44.2 (t), 35.6 (s), 31.9 (t), 30.6 (d), 28.8 (d), and 16.8 (q); mass spectrum, m/e (rel intensity) 136 (molecular ion, 24), 93 (32), 92 (100), and 79 (36). Anal. Calcd for $C_9H_{12}O$: m/e 136.0888. Found: m/e 136.0890.

4-Formyl-2-methyltricyclo[3.2.1.$0^{2,7}$]octan-3-one (6a). Sodium hydride (0.60 g, 25 mmol), ethyl formate (9.50 g, 12.8 mmol), ethanol (0.50 g, 10 mmol), and tricyclic ketone **5** (1.72 g, 12.6 mmol) were stirred at 25 °C for 42 h in diethyl ether (100 mL). The reaction mixture was extracted with 10% KOH (2 × 50 mL) and the organic

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