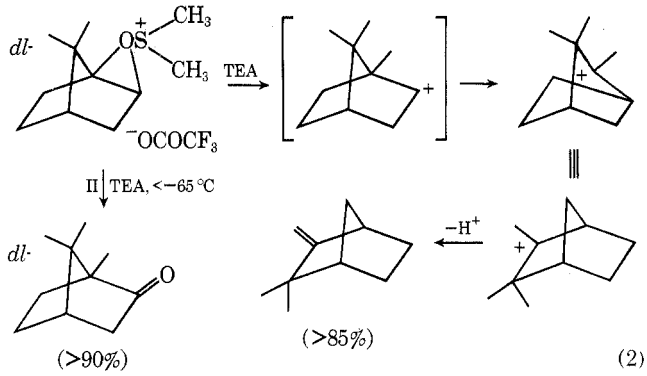
possible to oxidize alcohols which form stable sulfonium salts *only* at low temperatures. The oxidation of *dl*-isoborneol is a good illustration of this point. The sulfonium salt (II) is solvolyzed at room temperature (or above) and camphene, the rearrangement–elimination product, is obtained when procedure C (room temperature addition of TEA) is employed. But *dl*-camphor, the anticipated oxidation product, can still be obtained in high yield by addition of TEA at low temperature (<−65 °C). The reaction course is depicted as follows (eq 2):



(2)

Experimental Section

Procedures for Oxidation of Alcohols. Procedure A. To a solution of dry Me_2SO (20 mmol) in distilled dry CH_2Cl_2 (10 ml) cooled below −65 °C with a dry ice–acetone bath, TFAA (15 mmol) in CH_2Cl_2 (5 ml) was added with efficient mechanical stirring in ca. 10 min. After 10 min below −65 °C, a solution of an alcohol (10 mmol) in CH_2Cl_2 (5–10 ml) was added to the mixture in ca. 10 min. The rate of addition of TFAA or alcohol was controlled to keep the temperature below −65 °C. The mixture was stirred below −65 °C for 30 min, followed by addition of TEA (4 ml) dropwise in ca. 10 min. The temperature was maintained below −65 °C until addition of TEA was complete. The cooling bath was then removed and the reaction mixture was allowed to warm up to room temperature (ca. 40 min), then washed with H_2O (20 ml) and the aqueous layer was backwashed with CH_2Cl_2 (5 ml). The combined organic solutions were subjected to GLC analysis as previously reported.[2]

Procedure C. This procedure was identical with procedure A through the addition of alcohol. Stirring was continued for an additional 5 min below −65 °C; the dry ice bath was removed and the stirred mixture was allowed to warm up to room temperature (ca. 40 min). After another 30 min of stirring, at room temperature, TEA (4 ml) was added dropwise (ca. 10 min) at room temperature. The remainder of the workup was the same as in procedure A.

2,4-Dinitrophenylhydrazones.[2] The precipitate was filtered, washed, and dried. Ir and melting point were compared with those of authentic samples.

Isolation of Carbonyls. Ether was added to the reaction mixture which was then washed with dilute HCl, Na_2CO_3, and H_2O in succession. The organic layer was dried over magnesium sulfate and, after evaporation of solvent, a crude product was obtained as a residue. The pure product was isolated either by distillation or short-column chromatography on silical gel with petroleum ether/CH_2Cl_2 as eluent. Physical characteristics (ir, NMR, melting point) were compared with those of authentic samples of carbonyls.

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Registry No.—*cis*-**1**, 937-05-3; *trans*-**1**, 21862-63-5; **2**, 3835-64-1; **3**, 464-07-3; **4**, 75-84-3; **5**, 600-36-2; **6**, 5337-72-4; **7**, 507-70-0; **8**, 24393-70-2; **9**, 497-37-0; *endo*-**10**, 497-36-9; **11**, 700-57-2; **12**, 770-71-8; *cis*-**13**, 7443-70-1; **14**, 7443-52-9; 4-*tert*-butylcyclohexanone DNP, 54532-12-6; 2,2-dimethyl-1-phenyl-1-propanone DNP, 59830-27-2; 3,3-dimethyl-2-butanone DNP, 964-53-4; 2,2-dimethylpropanol DNP, 13608-36-1; 2,4-dimethyl-3-pentanone DNP, 7153-35-7; 2,6-dimethylcyclohexanone DNP, 5074-27-1; 2-bornanone DNP, 2628-66-2; *dl*-2-bornanone DNP, 53567-66-1; camphene, 79-92-5; 2-norbornanone DNP, 3281-03-6; 2-adamantanone DNP, 10535-35-0; 1-adamantanecarboxaldehyde DNP, 18220-81-0; 2-methylcyclohexanone DNP, 5138-30-7.

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Ferrocenecarboxylic Acids from Substituted Ferrocenes. A Convenient and Versatile Oxidation Method[1]

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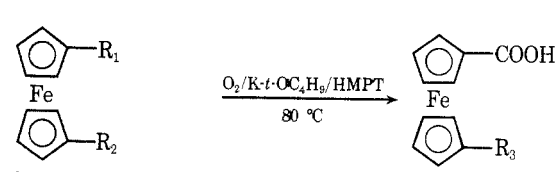
There are only very few examples known in which ferrocenecarboxylic acids can be prepared via side chain oxidation of ferrocenes. The oxidation is limited to ferrocenecarboxaldehydes[2] and acetylferrocenes[3,4] giving only low yields of carboxylic acids.

We now wish to report a convenient and versatile method for the oxidation of hydroxymethyl, formyl, acetyl, and *N,N*-dimethylaminomethyl substituted ferrocenes to ferrocenecarboxylic acids. The oxidation is performed with molecular oxygen at 80 °C in hexamethylphosphoric triamide (HMPT) as a solvent and in the presence of potassium *tert*-butoxide. The results which are summarized in Table I were obtained after a reaction time of 24 h by using 10 equiv of potassium *tert*-butoxide per equivalent of substituent to be oxidized. Lowering the amounts of base gave inferior yields and required longer reaction times.



1a, $R_1 = CH_2OH$; $R_2 = H$
b, $R_1 = CHO$; $R_2 = H$
c, $R_1 = COCH_3$; $R_2 = H$
d, $R_1 = CH_2N(CH_3)_2$; $R_2 = H$
e, $R_1 = R_2 = CH_2OH$
f, $R_1 = R_2 = CHO$
g, $R_1 = R_2 = COCH_3$

2a, $R_3 = H$
b, $R_3 = COOH$

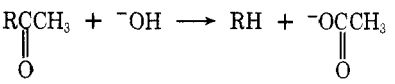
The oxidation reaction with hydroxymethyl, formyl, and acetyl substituted ferrocenes proceeded with almost quantitative conversions. The lower yields of ferrocenecarboxylic acids (**2a,b**) (see Table I) obtained from the oxidation of ac-

Table I. Ferrocenecarboxylic Acids via Oxygenation

Reaction	Yield,[a] %	Reaction	Yield,[a] %
1a → 2a	80	1e → 2b	83
1b → 2a	86	1f → 2b	86
1c → 2a	51	1g → 2a	34
1d → 2a	25	2b	17

[a] Satisfactory analytical and ir data were obtained.

etylferrocenes are due to a keto cleavage which acetylferrocenes partially can undergo in the presence of strong base.[5]



Thus, oxidation of **1c** gave 40% ferrocene and only 51% **2a.** The oxidation of **1g** yielded 26% ferrocene, 34% **2a,** and only 17% **2b.**

The high conversions of **1a–c** and **1e,f** are very surprising because the corresponding oxidation of mono- and dimethylferrocenes to ferrocenecarboxylic acids never yielded more than 25%.[6] As we could show the lower yields are due to an inhibiting effect caused by oxidation products of HMPT.[7]

Obviously this inhibiting effect does not exist during oxidation of hydroxymethyl, formyl, and acetyl substituted ferrocenes but seems to exist during oxidation of *N,N*-dimethylaminomethylferrocene (**1d**) which yielded only 25% of **2a.** This result leads to the assumption that oxidation products of *N,N*-dimethylamino groups, which are present in HMPT and in **1d,** may inhibit the base-catalyzed oxidation. The inhibiting effect is under further investigation.

Experimental Section

General Procedure. To a solution of freshly sublimed potassium *tert*-butoxide (150 mmol, for one substituent to be oxidized) in 110 ml of freshly distilled HMPT was added under inert atmosphere a solution of **1a–g** (15 mmol) in 20 ml of HMPT. After stirring for 30 min at room temperature dry oxygen was bubbled through the mixture which then was heated to 80 °C for 24 h. The reaction products were poured on ice, and the resulting alkaline solution was extracted with ether. The aqueous phase was acidified with dilute hydrochloric acid. Ferrocenecarboxylic acids **2a,b** precipitating upon acidification were filtered off and dried over phosphorus pentoxide. The acid solution was extracted with ether, and the compounds **2** were obtained after evaporation of the ether extracts. Recrystallization from ethanole was not necessary (**2a,** mp 202–204 °C, lit.[2] mp 205–210 °C; **2b,** mp 250 °C dec, lit.[3b] mp 250 °C dec). Mixtures from **2a** and **2b,** obtained from the oxidation of 1,1′-diacetylferrocene, can be separated by extraction with hot benzene, in which the monocarboxylic acid is soluble.

Registry No.—**1a,** 1273-86-5; **1b,** 12093-10-6; **1c,** 1271-55-2; **1d,** 1271-86-9; **1e,** 1291-48-1; **1f,** 1271-48-3; **1g,** 1273-94-5; **2a,** 1271-42-7; **2b,** 1293-87-4.

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Hydrogenation of Cyclohexene Catalyzed by First Row Transition Metal Stearates

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Among the most unusual and promising catalysts for homogeneous hydrogenation of olefins and aromatics are the transition metal stearates reported by Tulupov.[1–4] A good brief summary can be found in James' book[5] and Tulupov has published on the kinetics and mechanism of the reaction[6] and on the interaction of the metals with cyclohexene[7] in addition to two reviews.[8] We have attempted to repeat some of Tulupov's work and failed.

Briefly, Tulupov reported the reduction of cyclohexene in ethanol by hydrogen at ca. 1 atm at room temperature in the presence of stearate salts of Ni(II), Cu(II), Co(II), Cr(III), Fe(III), Sc(III), Ti(IV), and Zn(II). He also reports the hydrogenation of benzene catalyzed by stearate salts of Ni(II), Co(II), Fe(III), and Pb(II). There is little precedent for these observations in the literature. It is well known that Cu(I) carboxylate salts catalyze the reduction of benzoquinone[9] in quinoline and this reaction has been studied by two groups.[10,11] Also Rh(II) acetate is known to catalyze the hydrogenation of olefins in a variety of solvents.[12] A number of salts reported as active in ethanol by Tulupov have been reported to be inactive in aqueous systems,[13] consistent with Tulupov's claim of inhibition by water. Neither the Rh(II) nor Cu(I) work serves as confirmation of Tulupov's reports since the Cu(I) system was run in a solvent very different from ethanol and Tupulov did not study any rhodium systems. A thorough literature search yielded no reports of attempts to repeat Tulupov's studies.

Results

A number of stearate salts were prepared using Koenig's procedure,[14] the same one used by Tulupov. After a number of washings, pure salts having acceptable analyses were obtained. When we attempted to dissolve the Ni(II) stearate in anhydrous ethanol (Tulupov[2] reports the solubility as 4.21×10^{-3} M/l.), the ethanol remained colorless and all the salt was recovered by filtration. Two very tiny crystals of Ni(II) stearate were placed in an Erlenmeyer flask with ca. 100 ml of ethanol and allowed to stand for 6 h with occasional shaking. They did not dissolve. Warming the flask until the Ni(II) stearate melted did not result in any room temperature solubility. Similar observations were made with Cu(II) stearate (reported[3] solubility 4.02×10^{-4} M/l.) except that we did note some small solubility in hot ethanol. Koenig[14] reports that these two salts are insoluble in methanol but soluble in amyl alcohol.

A number of attempts were made to hydrogenate cyclohexene and some of them are reported in Table I. All reactions were run in Parr hydrogenators in which other catalytic hydrogenations had successfully been carried out. In no case was any reaction observed. With reaction no. 7, assuming that Tulupov's[3] reported reaction rate in ethanol would be unchanged in isobutyl alcohol, we can calculate a pressure drop of ca. 5.3 psi under our reaction conditions. We could detect a pressure drop of ca. 0.2 psi. The reactions were run with commercial anhydrous ethanol and with ethanol dried by refluxing over Mg and distillation under dry N_2 onto molecular sieves (3A). Two different batches of sodium stearate were used. The cyclohexene gave only two peaks on gas chromatography; one, having a slightly larger retention time than