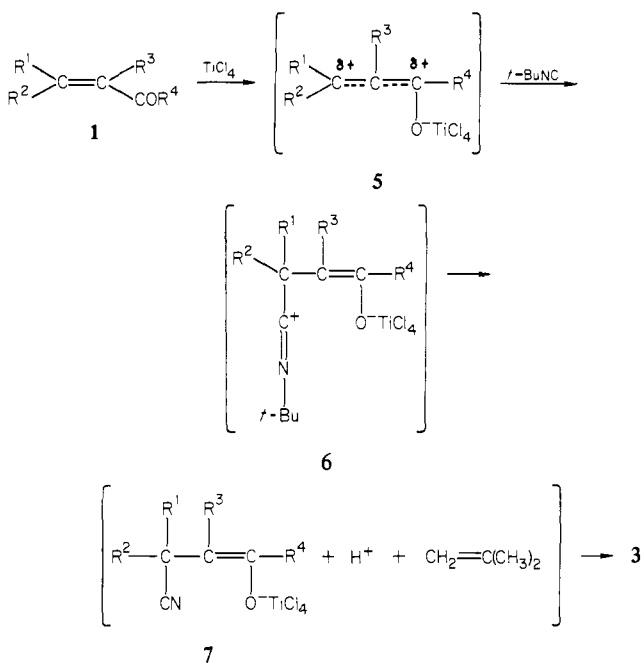
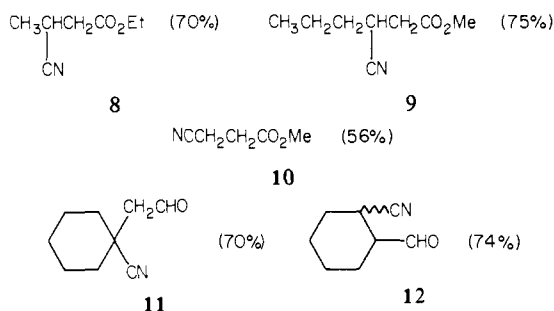


Scheme II



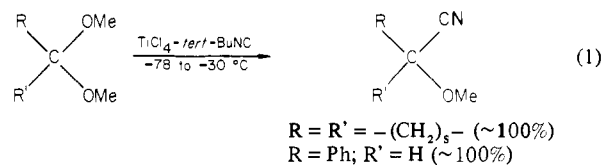
The successful hydrocyanation with *tert*-butyl isocyanide may lend support to the proposal that the corresponding metal isocyanide in equilibrium with metal cyanide might be the true cyanating agent for the hydrocyanation with organoaluminum cyanide^{1,7} and cyanotrimethylsilane.^{2,8}

Conjugate hydrocyanations of α,β -unsaturated aldehydes and esters, which were not satisfactory by means of the TiCl_4 -*tert*-butyl isocyanide, were achieved⁹ in moderate yields by the ethylaluminum dichloride-*tert*-butyl isocyanide system and by the aluminum trichloride-*tert*-butyl isocyanide system, respectively, as shown, e.g., by 8-12. However, the conjugate hydrocyanations



of α,β -unsaturated aldehydes such as crotonaldehyde and 2-hexenal were accompanied by product mixtures, which may be due to the competing 1,2-addition of *tert*-butyl isocyanide to the aldehyde carbonyl.

In conjunction with the 1,2-addition of *tert*-butyl isocyanide to the carbonyl group, we recently found that the TiCl_4 -*tert*-butyl isocyanide system is able to serve as a mild cyanating agent of ketal and acetal (see eq 1). The conjugate hydrocyanation of



α,β -unsaturated ketones in this study is very unique and useful because of the high yield and the mild conditions in addition to not needing dangerous cyanide sources.

Registry No. 1a, 141-79-7; 1b, 15932-80-6; 1c, 1193-18-6; 1d, 78-59-1; 1e, 874-68-0; 1f, 930-68-7; 1g, 1196-55-0; 1h, 4087-39-2; 2, 7188-38-7; 3a, 33235-13-1; 3b, 83268-53-5; 3c, 33235-14-2; 3d, 7027-11-4; 3e, 83268-54-6; *cis*-3f, 83268-55-7; *trans*-3f, 83268-56-8; *cis*-3g, 200-83-1; *trans*-3g, 3954-08-3; *cis*-3h, 880-38-6; *trans*-3h, 943-95-3; 8, 22584-00-5; 9, 83268-58-0; 10, 4107-62-4; 11, 29940-82-7; 12, 83268-59-1; TiCl_4 , 7550-45-0; 1,1-dimethoxycyclohexane, 933-40-4; benzaldehyde dimethyl acetal, 1125-88-8; 1-methoxy-1-cyclohexanecarbonitrile, 83268-57-9; α -methoxybenzeneacetonitrile, 13031-13-5; ethyl crotonate, 2396-77-2; methyl acrylate, 96-33-3; cyclohexylideneacetaldehyde, 1713-63-9; 1-cyclohexene-1-carboxaldehyde, 1192-88-7; aluminum trichloride, 7446-70-0; ethylaluminum dichloride, 563-43-9.

$[\text{Fe}_3\text{O}(\text{OCOR})_6\text{L}_3]^+$ -Catalyzed Epoxidation of Olefinic Alcohol Acetates by Molecular Oxygen[†]

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Received June 1, 1982

Selective monooxygenation of complicated olefins by molecular oxygen to yield epoxides is one of the crucial problems in connection with studies on both biological processes¹ and organic synthesis. Many kinds of transition metals are well-known to catalyze the epoxidation of olefins with hydroperoxides.² Little is known, however, about efficient catalytic epoxidation by molecular oxygen except for that of simple olefins such as ethylene.³

A plausible mechanism for the silver-catalyzed epoxidation of ethylene includes the participation of at least two metal atoms in the activation of an oxygen molecule.⁶ In addition, the oxygenase tyrosinase has recently been found to possess a binuclear metal-active site.⁷ These facts suggested to us the use of polynuclear transition-metal complexes as catalysts for the epoxidation of olefins by molecular oxygen.

To attain this purpose, we selected $(\mu_3\text{-oxo})$ triiron cluster complexes as catalysts, since a ruthenium analogue, $[\text{Ru}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]^+$, is capable of reversibly binding the central triply bridging oxygen atom.⁸ The characteristic features of the epoxidation of olefins by molecular oxygen with the $(\mu_3\text{-oxo})$ triiron

[†] Dedicated to Emeritus Professor Takeo Sakan on the occasion of his 70th birthday.

(1) For a review, see: Hamberg, M.; Samuelsson, B.; Björkhem, I.; Danielsson, H. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974; Chapter 2.

(2) For reviews, see: (a) Hiatt, R. In "Oxidation"; Augustine, R. L., Trecker, D. J., Eds.; Marcel Dekker: New York, 1971; Vol. 2, Chapter 3. (b) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* 1979, 12, 63.

(3) For a review, see: Mayo, F. R. *Acc. Chem. Res.* 1968, 1, 193. Metal-catalyzed epoxidation of cyclohexene⁴ and styrene⁵ by molecular oxygen have been reported, but the efficiency of the catalyst and selectivity of the reaction are low.

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(7) Winkler, M. E.; Lerch, K.; Solomon, E. I. *J. Am. Chem. Soc.* 1981, 103, 7001.

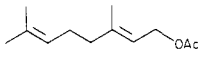
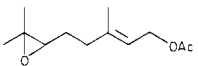
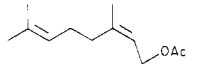
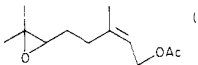
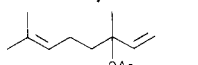
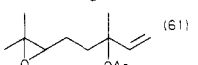
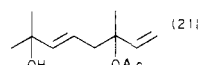
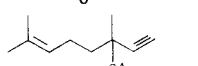
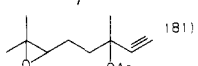
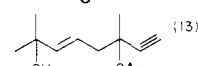
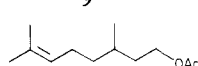
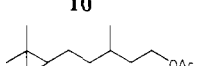
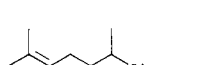
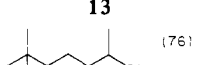
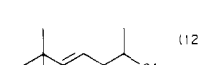
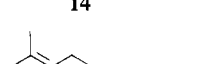
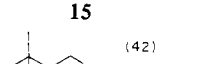
(8) Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1972, 1570.

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(8) (a) Evans, D. A.; Hoffmann, J. M.; Truesdale, L. K. *J. Am. Chem. Soc.* 1973, 95, 5822. (b) Utimoto, K.; Horie, T. *Tetrahedron Lett.* 1982, 237.

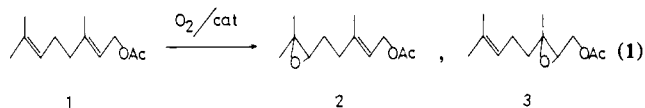
(9) Conjugate hydrocyanations of α,β -unsaturated aldehyde and ester were carried out by slowly adding a solution of *tert*-butyl isocyanide (2 mmol) in methylene chloride (6 mL) to a solution of aldehyde (1 mmol)- EtAlCl_2 (1 mmol) or ester (1 mmol)- AlCl_3 (1 mmol) in methylene chloride (3 mL) at room temperature over 7 h. 8: IR (neat) 2242, 1738 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 0.92 (t, 3 H), 1.25-1.67 (m, 4 H), 2.38-2.59 (m, 2 H), 2.62-3.03 (m, 1 H), 3.56 (s, 3 H). 11 (bp 72 °C (0.5 mmHg)): IR (neat) 2226, 1728 cm^{-1} ; NMR (CDCl_3) δ 0.75-2.38 (m, 10 H), 2.50 (d, 2 H, $J = 2.6$ Hz), 9.78 (t, 1 H, $J = 2.6$ Hz). 12 (bp 64 °C (0.5 mmHg)): IR (neat) 2244, 1728 cm^{-1} ; NMR (CDCl_3) δ 0.75-3.28 (m, 10 H), 9.57 and 9.58 (two s, 1 H).

Table I. $[\text{Fe}_3\text{O}(\text{piv})_6(\text{MeOH})_3]^+$ -Catalyzed Epoxidation of Olefinic Alcohol Acetates by Molecular Oxygen

substrates	cat ratio, mol %	conv, %	products (yield %)
	2.1	82	
	2.1	52	
	1.2	69	 
	1.8	70	 
	1.3	68	
	1.4	66	 
	0.6	16	

cluster catalysts are as follows: (1) Comparably complicated olefins such as geranyl acetate are effectively converted into the corresponding epoxides. (2) The regioselectivity of the reaction resembles that of oxidation with peracids.⁹ (3) Equimolar amounts of oxygen molecule seem to be required for the monoepoxidation of the olefins to epoxides.

When geranyl acetate (**1**, eq 1) was treated with $[\text{Fe}_3\text{O}-$

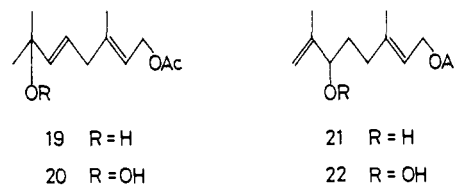


$(\text{piv})_6(\text{MeOH})_3]\text{Cl}$ (piv = $\text{OCOC}(\text{Me})_3$,¹⁰ 2–3 mol%) under oxygen (1 atm) at 60 °C for 20 h, 6,7-epoxygeranyl acetate (**2**) was produced in 87% yield, and no isomeric 2,3-epoxide (**3**) could be detected.¹² As shown in Table I, olefinic acetates **4**, **6**, **9**, **12**, **14**, and **17** were similarly oxidized to the corresponding epoxides,¹³ which were, in some cases, accompanied by “ene” reaction products, e.g., **8**, **11**, and **16**.¹⁴ The results with monoterpene

acetates **1**, **4**, and **6** show that the regioselectivity of the reaction described here resembles that of peracid oxidation but is opposite to that of Sharpless's epoxidation employing *t*-BuOOH/ $\text{VO}(\text{acac})_2$.¹⁷

Other (μ_3 -oxo)triiron complexes such as $[\text{Fe}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3](\text{OAc})^{18}$ and $[\text{Fe}_3\text{O}(\text{OAc})_6\text{py}_3]\text{Cl}^{18}$ were also effective catalysts for the epoxidation, but mononuclear ferric compounds such as FeCl_3 were ineffective under a variety of conditions. The epoxidation did not, of course, proceed without the catalyst. Furthermore, $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ and $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, which catalyze the epoxidation of styrene,⁵ exhibited scarcely any catalytic activity in the oxidation of **1** under our reaction conditions.

These catalytic epoxidations were inhibited by the addition of a hindered phenol such as 2,6-di-*tert*-butyl-*p*-cresol. This fact suggested a possible mechanism for the reaction involving the primary formation of an allylic hydroperoxide, which then reacts with further substrate to give the epoxide, as has been proposed for the epoxidation of tetramethylethylene catalyzed by $\text{M}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ ($\text{M} = \text{Rh}, \text{Ir}$).¹⁹ With **1**, the corresponding intermediary hydroperoxide would be **20** and/or **22**, which are



easily prepared by the sensitized photooxygenation of **1**.¹⁶ However, neither the hydroperoxides **20** and **22** nor *tert*-butyl hydroperoxide were found to oxidize **1** in the presence of the (μ_3 -oxo)triiron complex under anaerobic conditions. This result rules out a mechanism involving hydroperoxides, although radical

(9) Mousseron-Canet, M.; Mousseron, M.; Levallois, C. *Bull. Soc. Chim. Fr.* **1964**, 297.

(10) The complex was prepared from iron(III) chloride and sodium pivalate by the literature method,¹¹ which was accompanied by some difficulty in isolation of the complex. Repeated crystallization of initially formed precipitates from chloroform-methanol furnished the desired complex as orange-yellow crystals, which displayed a mass spectrum identical with that of the literature.¹¹

(11) Blake, A. B.; Fracer, L. R. *J. Chem. Soc., Dalton Trans.* **1975**, 193.

(12) Typical experiment was as follows: a mixture of 300 mg of **1** and 30 mg of $[\text{Fe}_3\text{O}(\text{piv})_6(\text{MeOH})_3]\text{Cl}$ was stirred *without solvent* at 60 °C for 20 h under oxygen (1 atm) followed by silica gel chromatography (eluant CH_2Cl_2) to give 53 mg of unreacted **1**, 231 mg of **2** (87% based on consumed **1**), and minor amounts of degradation products.

(13) Other simple mono- and disubstituted olefins such as styrene and β -methylstyrene were also found to be oxygenized to epoxides, though the efficiency was far less than those of the acetates cited in the table. The results of *trans*- β -methylstyrene and the *cis* isomer exhibited lack of the stereospecificity in the present epoxidation; although *trans*- β -methylstyrene gave only *trans* epoxide (23%), *cis*- β -methylstyrene yielded a mixture of *trans* and *cis* epoxides (36%, 5:1).

(14) Each epoxide could not be converted to the corresponding allylic alcohol under the reaction conditions. No isomeric allylic alcohols such as **21**¹⁵ could be detected in the reaction mixtures.

(15) Authentic allylic alcohols were synthesized according to the procedure of Dunphy.¹⁶

(16) Dunphy, P. J. *Chem. Ind. (London)* **1971**, 731.

(17) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136.

(18) Earnshaw, A.; Figgs, B. N.; Lewis, J. J. *J. Chem. Soc. A* **1966**, 1656.

(19) Lyons, J. E.; Turner, J. O. *J. Org. Chem.* **1972**, *37*, 2881.

species may play an important role elsewhere in the reaction.

The stoichiometry of reaction 1 as a function of time was followed by GLC analysis²⁰ and measurement of consumed oxygen gas. A striking characteristic of the reaction was that the molar ratio of the epoxide formed vs. the molecular oxygen consumed was close to unity throughout the reaction. In the present epoxidation, oxygen is consequently required in twice the ideal stoichiometry. We therefore looked for products other than **2** in the reaction of **1** and found several oxidative degradation products, among them 3-methyl-2-butenal and 2-hydroxypropanal. Control experiments showed that these degradation products derived from neither the epoxide **2**, the allyl alcohol **19** corresponding to **8**, **11**, and **16**, nor hydroperoxide **20**. These facts suggested that one atom of the oxygen molecule is used for the epoxidation and the other atom is consumed in oxidative degradation of the substrate. These phenomena also appear to be characteristic of the silver-catalyzed epoxidation of ethylene.⁶

Although further systematic studies are necessary to clarify the mechanism of the reaction, the reaction described here may be a new type of epoxidation by molecular oxygen and is the first example of nonenzymatic iron-catalyzed regiospecific oxygenation of complicated olefins by molecular oxygen.

Registry No. **1**, 105-87-3; **2**, 23519-09-7; **4**, 141-12-8; **5**, 63707-79-9; **6**, 115-95-7; **7**, 41610-76-8; **8**, 83221-21-0; **9**, 29171-21-9; **10**, 77743-54-5; **11**, 83221-22-1; **12**, 150-84-5; **13**, 1787-98-0; **14**, 19162-00-6; **15**, 83221-23-2; **16**, 83221-24-3; **17**, 1191-16-8; **18**, 83221-25-4; **20**, 33766-44-8; **22**, 33766-45-9; [Fe₃O(piv)₆(MeOH)₃]Cl, 55216-31-4; [Fe₃O(OAc)₆(H₂O)₃](OAc), 60797-92-4; [Fe₃O(OAc)₆Py₃]Cl, 69554-73-0; FeCl₃, 7705-08-0.

(20) GLC analysis was carried out by using a 20% XE-60 column (2 m) at 160 °C.

Relationship between the Freundlich Adsorption Constants K and $1/N$ for Hydrophobic Adsorption

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A good linear relationship has been obtained between the logarithm of K and $1/N$ of the Freundlich adsorption constants for hydrophobic adsorption. The linear equation is applicable to many adsorbent-adsorbate systems.

We now consider the adsorption of hydrocarbons onto a hydrophobic adsorbent such as activated carbon. For such adsorption the Polanyi adsorption potential theory may be applied as follows.¹⁻⁴

The adsorption of solute takes place by the precipitation of the solute on the surface with potential estimated as

$$\epsilon_{s1} = RT \ln (C_s/C) \quad (1)$$

where C_s and C are the saturated and the equilibrium concentrations. We assume that the relation between the adsorption potential (ϵ_{s1}) and the volume of solute adsorbed (W) is given by the expression

$$W = W_0 \exp[-m(\epsilon_{s1}/V_s)] \quad (2)$$

where W_0 is the limiting volume of adsorption space, V_s is the molar volume of solute, and m is a parameter of the distribution function. This equation is another form of the Freundlich equation of the adsorption isotherm since it can easily be brought to the form

$$W = W_0 \exp\left(-\frac{mRT}{V_s} \ln C_s/C\right) = W_0(C/C_s)^{mRT/V_s} = KC^{1/N} \quad (3)$$

where

$$K = W_0(1/C_s)^{mRT/V_s} \quad (4)$$

and

$$1/N = mRT/V_s \quad (5)$$

By taking logarithms, eq 4 can be written in the form

$$\log K = \log W_0 - (mRT/V_s) \log C_s \quad (6)$$

It is well-known that the logarithm of the solubility of hydrocarbon in water is a linear function of the hydrocarbon molar volume:⁵

$$\log C_s = aV_s + b \quad (7)$$

where a and b are constants. By combining eq 5-7, we obtain

$$1/N = -(1/b) \log K + (1/b)(\log W_0 - amRT) \quad (8)$$

This equation indicates that a linear relationship is set up between the logarithm of K and $1/N$ of the Freundlich adsorption constants. The equation has been applied to actual adsorption data in order to examine the validity of eq 8. We have measured the adsorption isotherms of 139 organic compounds (including alcohols, ethers, ketones, aldehydes, amines, esters, fatty acids, amino acids, aromatics, saccharides, glycols, and surfactants, etc.) from aqueous solution onto an activated carbon (Pittsburgh Activated Carbon Co., grade CAL) at 25 °C.^{3,6-13} The isotherms have been approximated by the Freundlich equation with the following units:

$$\log X = \log K + (1/N) \log C \quad (9)$$

where X is the amount of solute adsorbed (mg/g of adsorbent) and C is the equilibrium concentration of solute (mg/L). When the K value is expressed in weight unit instead of volume unit, eq 8 is changed to the following equation:

$$1/N = -(1/b) \log K + (1/b)(\log W_0 + \log \rho + 3 - amRT) \quad (10)$$

where $X = 1000\rho W$, ρ is the density of adsorbate (g/mL), and W_0 and W are expressed in mL/g of adsorbent. The slope of the line expressed by eq 10 is independent of the nature of adsorbent and adsorbate. Assuming that the density of each adsorbate is nearly equal, the intercept of the line depends on the nature of adsorbent and is independent of adsorbate. Figure 1 shows a plot $\log K$ vs. $1/N$ for the 139 compounds. The line is from linear least-squares analysis of the 136 data points excluding three points

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