$$(\eta^5\text{-}C_5H_5)_2(H)Nb=CHOZr(H)(\eta^5\text{-}C_5Me_5)_2 + CO \longrightarrow$$

$$(\eta^5\text{-}C_5H_5)_2(CO)Nb\text{-}CH_2OZr(H)(\eta^5\text{-}C_5Me_5)_2 \qquad (6)$$

$$(\eta^5\text{-}C_5H_5)_2(H)Nb=CHOZr(H)(\eta^5\text{-}C_5Me_5)_2 + 2H_2 \xrightarrow{25°}$$

$$(\eta^5\text{-}C_5H_5)_2NbH_3 + (\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) \qquad (7)$$

$(\eta^5\text{-}C_5H_5)_2NbH_3$ and $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$ (eq 7).[28] The facility of reaction 7 vis-à-vis reaction 3 may be attributed to the availability of a tautomerization pathway for **8** which generates a formal 16-electron Nb(III) species capable of oxidatively adding H_2.

These new results bring into question the occurrence of an *intra*molecular hydride transfer for the rearrangement of $(\eta^5\text{-}C_5Me_5)_2ZrH_2(CO)$ to $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH)$. We are presently extending our studies of this reaction type to the zirconium carbonyl systems as well as to group 8 transition metal carbonyls.

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(23) NMR (toluene-d_8) at -3 °C: $[\eta^5\text{-}C_5H_5]$, s, δ 4.12 (5 H), and s, δ 4.24 (5 H); CHO, s, δ 13.27 (1 H); $[\eta^5\text{-}C_5(CH_3)_5]$, s, δ 1.93 (30 H); ZrH, s, δ 5.94 (1 H).
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(26) Whereas there could be some ambiguity concerning the origin of the hydrogen which was transferred to the carbonyl group in reaction 5, treatment of $(\eta^5\text{-}C_5H_5)_2Nb(H)(CO)$ with $[\eta^5\text{-}C_5(CD_3)_5]_2ZrD_2$ yields $(\eta^5\text{-}C_5H_5)_2(H)$-$Nb=CDOZr(D)[\eta^5\text{-}C_5(CD_3)_5]_2$. Thus, as in all other cases, this hydrogen originates at zirconium.
(27) Calcd for $C_{32}H_{43}O_2NbZr$: C, 59.70; H, 6.58; Zr, 14.17. Found: C, 59.36; H, 6.94; Zr, 14.33. NMR (benzene-d_6): $[\eta^5\text{-}C_5H_5]$, s, δ 4.72 (10 H); OCH$_2$ and ZrH, s, δ 5.23 (3 H); $[\eta^5\text{-}C_5(CH_3)_5]$, s, δ, 2.01 (30 H). IR (Nujol mull): $\nu(ZrH)$ 1553 cm^{-1}; $\nu(CO)$ 1126 cm^{-1}; $\nu(C=O)$ 1898 cm^{-1}.
(28) Treatment of $(\eta^5\text{-}C_5H_5)_2(H)Nb=CHOZr(H)(\eta^5\text{-}C_5ME_5)_2$ with excess D$_2$ (1 atm) yielded a mixture of $(\eta^5\text{-}C_5Me_5)_2Zr(H)_n(D)_{1-n}(OCH_mD_{3-m})$ ($n = 0$, 1; $m = 0$, 1, 2, 3), suggesting that scrambling of the carbene hydrogen with the D$_2$ atmosphere occurs during reaction 7.
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(30) Alfred P. Sloan Fellow, 1976–1978, and Camille and Henry Dreyfus Teacher–Scholar, 1977–1982.

Peter T. Wolczanski, Richard S. Threlkel[29]
John E. Bercaw*[30]

Contribution No. 5855
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
*Pasadena, California 91125*

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Intramolecular Dibromo Ketone–Iron Carbonyl Reaction in Terpene Synthesis

Sir:

The iron carbonyl promoted cyclocoupling reaction of polybromo ketones and unsaturated substrates provides a powerful tool for the synthesis of five- and seven-membered carbocycles.[1] Trapping of the reactive 2-oxyallyl–iron(II) species with 1,3-dienes in a [3 + 4] manner produces 4-cycloheptenones efficiently, whereas [3 + 2] cycloaddition across an olefinic linkage gives cyclopentanone derivatives. The intramolecular version of such transformations, if feasible, would allow direct, highly ordered construction of polycyclic frameworks from open-chain systems. Reported herein is a new entry to polycyclic terpenes utilizing this strategy.

Possible [3 + 2] type cyclization was inspired by a biogenetic hypothesis. The carbon skeleton of mono- and sesquiterpenes having a bicyclo[2.2.1]heptane system can be derived from acyclic terpene precursors formally by carbocation–olefin cyclization (eq 1)[2] and this biogenetic formulation prompted
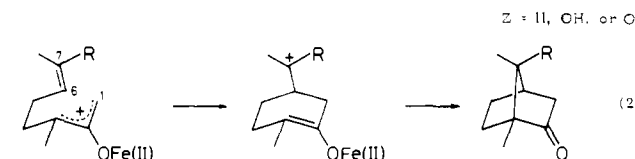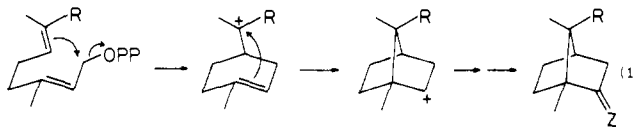

us to examine the chemical sequence involving an oxyallyl-iron(II) intermediate (eq 2) which could open a new route to camphor and campherenone[3,4] starting from geraniol (or nerol) and farnesol, respectively.

This plan has worked indeed well. When a mixture of the dibromo ketone **1** (obtained from geraniol) and Fe$_2$(CO)$_9$ (1:1.2 mol ratio) in benzene was heated in a pressure bottle at
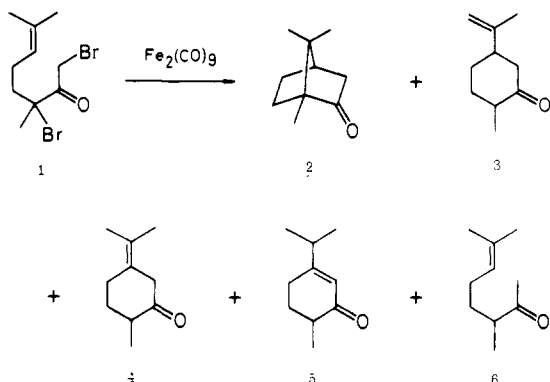
100-110 °C for 1.5 h, a C_{10} fraction was obtained in up to 70% yield (eq 3). The major component (54% of this fraction) was (±)-camphor (2). In addition, (±)-dihydrocarvone (3) (20%, 1:2.5 cis:trans), 4 (~4%), (±)-carvenone (5) (10%), and 6 (4-7%) were formed. Several minor components (total ~6%) remained unidentified.

In a similar fashion, reaction of the dibromo ketone (E)-7 (prepared from (E,E)-farnesol) and Fe(CO)$_5$ (1:1 mol ratio) in benzene at 100 °C afforded a 2:1 mixture of (±)-campherenone (8) and (±)-epicampherenone (9) in 58% yield (eq 4). The reaction using the stereoisomer, (Z)-7, produced a 1:2 mixture of 8 and 9.
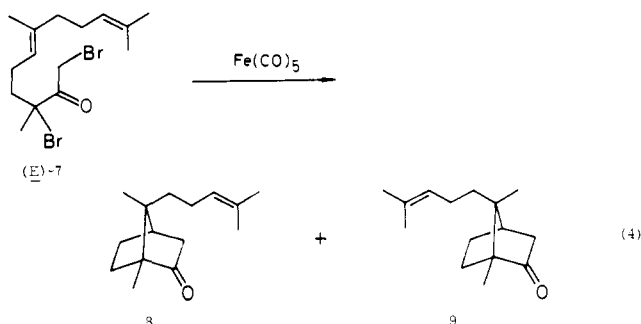
The ease with which the intramolecular [3 + 2] reaction takes place is affected profoundly by the substitution pattern around the olefinic bond as well as length of the methylene chain that links the double bond and dibromo ketone moiety. Apparently the feasibility of the biogenetically patterned acyclic to bicyclic conversion of eq 2 is based on the high stability of the zwitterionic intermediate that plays a crucial role in the stepwise cycloaddition; the regioselective C(1)-C(6) bonding leaves a positive charge on the tertiary carbon, C(7), and concurrently produces a fully substituted enolate moiety.[5-7] Electrophilic cyclization in the oxyallyl species derived from 7 is occurring selectively across the internal, C(6)-C(7) double bond rather than the C(10)-C(11) bond. Attempted reaction of 10-12 failed to afford the desired bicyclic ketones.
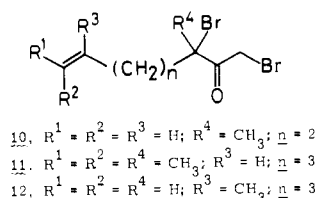
The intramolecular [3 + 4] reaction permits the direct synthesis of an oxidoperhydroazulene structure that is the basic skeleton involved in naturally occurring daucon,[8] ambrosic acid,[9] germacrol,[10] etc. For example, when a mixture of the dibromo ketone 13 and Fe$_2$(CO)$_9$ (1:1.5 mol ratio) in benzene

was heated at 80 °C for 3 h, the oxatricyclic ketone 15 was obtained in 41% yield (eq 5). Similarly reaction of 14 and Fe$_2$(CO)$_9$ produced 16 (38%). The stereochemistry of 16 was substantiated by converting to 17 by sequential treatment with
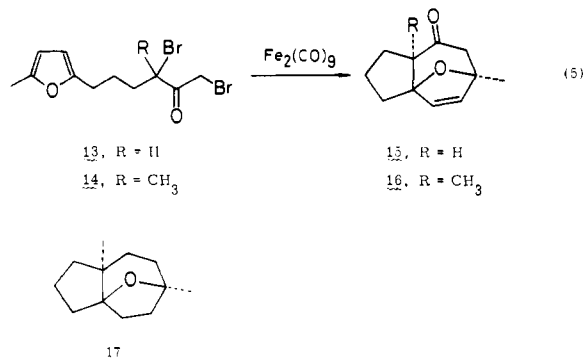
H_2 over PtO_2 in ethyl acetate, tosylhydrazine in benzene, catecholborane in $CHCl_3$, and finally $CH_3COONa\cdot3H_2O$;[11] in the Eu(fod)$_3$-aided NMR spectrum of 17, the singlet due to the angular methyl protons moved downfield more slowly than the other proton signals.[12]

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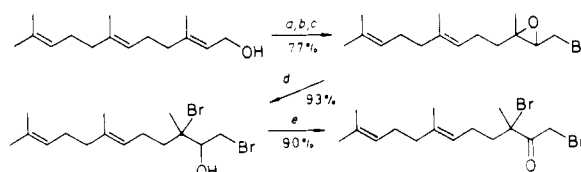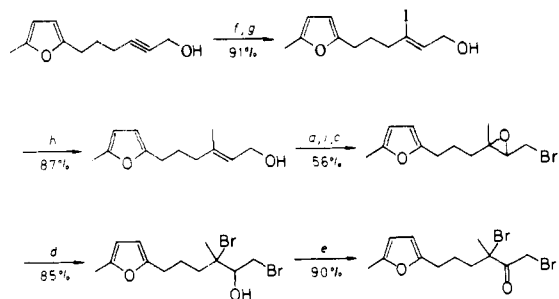
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(16) Address correspondence to Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822.

R. Noyori,* M. Nishizawa, F. Shimizu, Y. Hayakawa

Department of Chemistry, Nagoya University
Chikusa, Nagoya 464, Japan

Keiji Maruoka, Shinsaku Hashimoto
Hisashi Yamamoto,*[16] Hitosi Nozaki

Department of Industrial Chemistry, Kyoto University
Yoshida, Kyoto 606, Japan

Received December 5, 1977

Unexpected Reactions of Fe₂ and Fe in Low-Temperature Matrices

Sir:

The chemical reactions of metal atoms and small clusters in low-temperature matrices are being actively studied.[1] Such systems are models for both homogeneous and heterogeneous catalysis. Studies of metal vapors cocondensed with various substrates at 77 K are closely related.[2] Very little has been reported on the reactions of iron atoms. Iron vapors at 77 K react with cyclopentadiene to form ferrocene, and with 1,5-cyclooctadiene to give Fe(COD)₂.[2b]

The reaction of iron vapor condensed with nitrogen at 4–12 K showed that chemically bonded nitrogen was formed.[1b,3] Using a combination of Mössbauer and infrared spectroscopies, it was shown that the dimer, Fe₂, but not the monomer, Fe, reacted with nitrogen.[3] This is an unexpected result since Fe₂ is 30 kcal/mol more stable than 2Fe, owing to bond formation.[4]

In no case has a paraffin hydrocarbon been reported to react with metal atoms. Cr, V, and V₂ are inert in a number of hydrocarbon matrices, up to 80 K.[5] Ti is inert in cyclohexane, and Ni and Mg do not react with *n*-hexane. In fact, paraffin hydrocarbons are used as inert diluents in carrying out reactions at 77 K. Activated hydrocarbons, such as propylene, do react at 77 K. In some cases the reaction may be oxidative cleavage of the C–H bond.[2]

$$M + CH_3CH{=}CH_2 \rightarrow HMCH_2CH{=}CH_2 \quad (1)$$

The Mössbauer spectrum of isolated iron atoms, Fe, in a methane matrix has been reported to have the same isomer shift as in an inert gas matrix.[6] We have confirmed this result, but, on increasing the iron concentration in the matrix to form the dimer, quite unexpected results were found. The isomer shift of the dimer (−0.11 mm/s with respect to iron metal) was not observed. Instead new lines at +0.58 mm/s and +1.42 mm/s were found. This is in the range of diamagnetic, covalent compounds of iron for the low value, and ionic compounds of
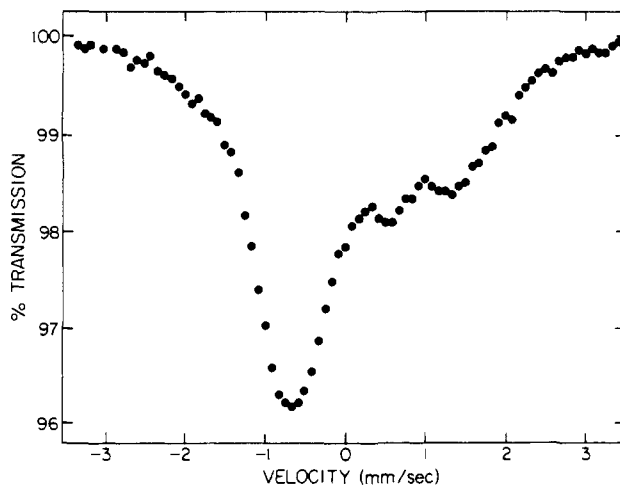

Figure 1. Mössbauer spectrum of solid methane matrix (20 K) with 2% ⁵⁷Fe (300 μg/cm² of iron). The matrix was deposited over a period of 20. The monomer absorbs at −0.75 mm/s.

iron(II) for the high value. Figure 1 shows the spectrum obtained.[7]

The Mössbauer spectrum is strong evidence that chemical reaction between Fe₂ and CH₄ has occurred. The most plausible reaction is oxidative cleavage of the C–H bond, e.g.,

$$Fe_2 + CH_4 \longrightarrow HFeFeCH_3 \text{ or } \underset{\overset{|}{H}}{FeFeCH_3} \quad (2)$$
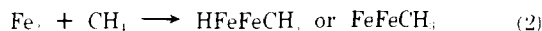
As many as two CH₄ molecules could react per Fe₂ unit, based on the expected change in oxidation state from iron(0) to iron(II).[8] A subsequent reaction might be

$$FeCH_3 \longrightarrow \underset{\overset{|}{H}}{Fe{=}CH_2} \quad (3)$$
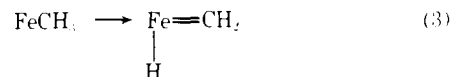
based on chemisorption studies of methane on iron films,[9] and on known reactions of transition metal alkyls.

A critical test of reactions 2 and 3 is the detection of Fe–H stretching vibrations in the 2000-cm⁻¹ region of the infrared spectrum. Accordingly, the same matrix-producing system used for the Mössbauer studies was used to produce matrices of iron and methane on an aluminum foil at 12 K.[10]

Matrices with iron concentrations of 0.1 to 1.0% showed well-defined absorption bands at 2046, 2027, 2014, and 2019 cm⁻¹. In addition, there are weak lines at 2041, 2038, and 1981 cm⁻¹. A matrix of pure methane shows no absorption in this region. If, as the Mössbauer spectra indicate, the iron dimer is the initiating structure for the iron–methane reaction, then the infrared absorption should be proportional to the square of the iron concentration. For methane/iron ratios from 500 to 5000 the intensities of all the above lines vary as the square of the iron concentration. At higher concentrations this quadratic relationship breaks down, probably owing to the formation of higher multimers. In matrices in which the methane is progressively diluted with argon, the bands at 2046, 2014, and 2019 cm⁻¹ decrease in intensity more rapidly than the band at 2027 cm⁻¹. This indicates that at least two products are formed with different Fe₂/CH₄ ratios.

When CD₄ is used as a matrix material instead of CH₄, the lines mentioned above all disappear. Presumably Fe–D stretching bonds could exist in the 1400-cm⁻¹ region, which is just outside of our present range of measurement. New lines are found in the iron-CD₄ matrix at 2220 and 2195 cm⁻¹. We take these to be C–D stretches in either CD₃ or CD₂ groups bound to iron. The corresponding bands in Fe–CH₄ matrices should occur at ~3000 cm⁻¹. Unfortunately, this region is very heavily obscured by background, but one new band appears at 2899 cm⁻¹.