

tion of more catalyst decreases the reaction yield. The same behaviour was observed when the oxidation was carried out under GoAgg II conditions<sup>11</sup>, where replacing the Zn powder and oxygen gas by hydrogen peroxide and Fe II by Fe III renders an homogeneous reaction mixture. Addition of catalytic amounts of picolinic acid (GoAgg III system)<sup>12</sup> accelerated markedly the reaction rate ( $\tau_{1/2}$  = 17 min for the catalyzed reaction,  $\tau_{1/2}$  > 100 min for the uncatalyzed reaction). This result implies that the mechanism of both the allylic ketonization and the functionalisation of saturated hydrocarbons by Gif-type reagents are related.

Gif chemistry does not involve carbon radicals<sup>13</sup>. Our theory proposes the formation of a carbon-iron(V) bond as the key step in the alkane activation process. We have recently shown that ligand coupling in the  $\mu$ -oxo-hydroperoxo di-iron intermediate affords an alkyl hydroperoxide, which is then fragmented to the ketone<sup>14</sup>. The results obtained in the Gif IV oxidation of (+)-car-3-ene show that the carbon-iron bond does not permit cyclopropyl ring opening. In contrast, radical autoxidation of compound **1** produced as major products derived from cyclopropane ring opening, (-)-*m*-mentha-4,6-dien-8-ol (**4**) and (+)-*p*-mentha-1,5-dien-8-ol (**5**)<sup>2</sup>. These two compounds were found as minor components (<1%) of the polar fraction from the Gif reaction (GC/MS analysis)<sup>8</sup>.

This results confirm the unique mildness and selectivity of Gif chemistry and supports our recently proposed theory<sup>14</sup>.

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8. A solution of (+)-car-3-ene (12.0 mmol) in pyridine (50 ml) containing  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (40 mg, 0.2 mmol) and zinc powder (2.62 g, 40 mg-at) was placed in an Erlenmeyer flask open to air. The reaction was started by adding glacial acetic acid (4.6 ml, 80 mmol), and the solution was stirred for 16 hrs at room temperature. The reaction mixture was cooled (ice-water bath), diluted with  $\text{Et}_2\text{O}$  and acidified with  $\text{H}_2\text{SO}_4$  (25%). The aqueous layer was extracted with  $\text{Et}_2\text{O}$ , the organic solutions combined, dried ( $\text{MgSO}_4$ ), and analyzed by gas chromatography.  $^{13}\text{C}$ -NMR data (at 20 MHz, ppm respect to TMS in  $\text{CDCl}_3$ ) for compound **2**: 14.8, 22.8, 24.0, 26.2, 28.9, 33.2, 126.3,

159.2, 197.1; for compound **3**: 14.5, 16.2, 22.3, 23.2, 26.5, 28.9, 34.5, 135.2, 143.1, 196.7; GC/MS data for compound **4**:  $m/z$  134 ( $\text{M}-\text{H}_2\text{O}^+$ ), 119, 91.

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11. A solution of compound **1** (6.0 mmol) and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.3 mmol) in pyridine (42.0 ml) was cooled in an ice-water bath.  $\text{H}_2\text{O}_2$  (30% in water, 2.5 ml, 22.0 mmol) was added dropwise. Reaction samples were worked up as in reference 7.
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## Synthesis of Poly(cyclohexene oxide) by $\text{WCl}_6$ - and $\text{MoCl}_5$ -Based Catalysts

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Various epoxides were polymerized with anionic, cationic, and coordination type catalysts.<sup>1</sup> The polymerization of cyclohexene oxide (CHO) have been carried out by  $\text{Et}_3\text{Al}$ ,<sup>2</sup>  $\text{Al}(\text{acac})_3\text{-Ph}_3\text{SiOH-alcohol}$ ,<sup>3</sup> aluminum complex-arylsilyl peroxide,<sup>4</sup>  $\text{Ti}(\text{O}-i\text{-Pr})_4\text{-ArOH}$ ,<sup>5</sup>  $\text{ZnEt}_2$ - (1R, 2S) ephedrine,<sup>6</sup> etc. However there have been no reports on the polymerization of CHO by W- and Mo-based catalysts.  $\text{WCl}_6$ - and  $\text{MoCl}_5$ -based catalysts exhibited a high catalytic activities on the metathesis polymerization of cycloolefins<sup>7</sup> and the polymerization of acetylene derivatives.<sup>8</sup> In recent years we reported the catalytic activities of  $\text{WCl}_6$ - and  $\text{MoCl}_5$ -based catalysts for the polymerization of acetylene derivatives carrying aromatic heterocycles and the cyclopolymerization of nonconjugated diynes.<sup>9,10</sup> The present article deals with the studies on the catalytic activity of  $\text{WCl}_6$ - and  $\text{MoCl}_5$ -based catalysts for the polymerization of CHO.

CHO (Aldrich Chemicals, 98%) was dried with  $\text{CaH}_2$  and fractionally distilled.  $\text{WCl}_6$  and  $\text{MoCl}_5$  (Aldrich Chemicals, re-sublimed, 99+%) were used without further purification.

$\text{EtAlCl}_2$  (Aldrich Chemicals, 25 wt% solution in toluene) was used as received. The polymerization was carried out under nitrogen atmosphere according to a procedure already described.<sup>9,10</sup>

Table 1 shows the results for the polymerization of CHO by  $\text{WCl}_6$ - and  $\text{MoCl}_5$ -based catalysts.  $\text{WCl}_6$  or  $\text{MoCl}_5$  itself shows no catalytic activity.  $\text{WCl}_6\text{-EtAlCl}_2$  and  $\text{MoCl}_5\text{-EtAlCl}_2$ , which were effective catalysts in the polymerization of some

**Table 1.** Polymerization of CHO by  $\text{WCl}_6$ - and  $\text{MoCl}_5$ -Based Catalysts<sup>a</sup>

| Exp. No. | Catalyst Systems <sup>b</sup><br>(mole ratio)    | M/C <sup>c</sup><br>(mole ratio) | Temp (°C) | P. Y. <sup>d</sup><br>(%) | $\bar{M}_n$ <sup>e</sup> | $\bar{M}_w$ <sup>e</sup> |
|----------|--|----------------------------------|-----------|---------------------------|--------------------------|--------------------------|
| 1        | $\text{WCl}_6$                                   | 500                              | -20       | 0                         | —                        | —                        |
| 2        | $\text{WCl}_6\text{-EtAlCl}_2$ (1 : 2)           | 500                              | -20       | 98                        | 5700                     | 19500                    |
| 3        | $\text{WCl}_6\text{-EtAlCl}_2$ (1 : 2)           | 250                              | -20       | 94                        | 7200                     | 25200                    |
| 4        | $\text{WCl}_6\text{-EtAlCl}_2$ (1 : 2)           | 500                              | 90        | 59                        | 6800                     | 21100                    |
| 5        | $\text{MoCl}_5\text{-EtAlCl}_2$ (1 : 2)          | 500                              | -20       | 99                        | 9800                     | 19700                    |
| 6        | $\text{MoCl}_5\text{-EtAlCl}_2$ (1 : 2)          | 250                              | -20       | 95                        | 11300                    | 27900                    |
| 7        | $\text{MoCl}_5\text{-(n-Bu)}_4\text{Sn}$ (1 : 2) | 500                              | -20       | 0                         | —                        | —                        |

<sup>a</sup>Polymerization was carried out in chlorobenzene for 24 hr. Initial monomer concentration was 2 M. <sup>b</sup>Mixture of catalyst and cocatalyst was aged at 30°C for 15 min before use. <sup>c</sup>Mole ratio of monomer to catalyst. <sup>d</sup>Methanol-insoluble polymer yield. <sup>e</sup>Determined by GPC in tetrahydrofuran solution using calibration curve for polystyrene.

acetylene derivatives<sup>11</sup> were also found to be very effective catalyst system in this polymerization of CHO. The mole ratio of monomer to catalyst (M/C) was relatively higher in comparison with those of the polymerization of acetylene derivatives by the same catalysts. The adequate mole ratio of cocatalyst to catalyst and the polymerization temperature were 2 and -20°C, respectively.  $\text{WCl}_6\text{-(n-Bu)}_4\text{Sn}$  catalyst systems shows no catalytic activities in this polymerization.

IR spectrum of poly (CHO) prepared by  $\text{WCl}_6\text{-EtAlCl}_2$  catalyst system shows the aliphatic C-H stretching frequency at 2858 and 2935  $\text{cm}^{-1}$  and it shows an absorption band at 1087  $\text{cm}^{-1}$  owing to C-O-C stretching frequency. The <sup>1</sup>H-NMR spectrum of poly (CHO) prepared by  $\text{WCl}_6\text{-EtAlCl}_2$  catalyst system shows the peaks at 3.2 and 3.8 ppm due to the protons of carbon adjacent to the ether linkage. The peaks between 1.2 and 2.0 ppm is assigned to be the protons of methylene carbons. The number average molecular weight ( $\bar{M}_n$ )s of the resulting poly (CHO) were ranged from 5700 to 11300. The polydispersity ( $\bar{M}_w/\bar{M}_n$ )s were ranged from 2.01 to 3.50. Conclusively  $\text{WCl}_6\text{-EtAlCl}_2$  and  $\text{MoCl}_5\text{-EtAlCl}_2$  were found to be very effective catalyst systems for the polymerization of CHO.

A more detailed description of these polymerization, as well as characterization of the resulting poly (CHO), will be discussed elsewhere.

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## A Practical Synthetic Route to Tricyclo [4.3.0.0<sup>1,5</sup>]nonane Derivatives

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The transitory formation of cyclopropanes has been often employed in terpene synthesis because their transformation enables otherwise synthetically difficult compounds to be accessible. Cyclopropanes are cleaved reductively or under acidic conditions to afford methyl or functionalized methylene groups.<sup>1</sup> Acid-mediated ring opening of  $\alpha$ -hydroxycyclopropanes provides a route to chain lengthening.<sup>2</sup> The most versatile chemistry in such transformations of cyclopropyl derivatives certainly stems from cyclopropyl ketones derived from diazoketones and alkenes intramolecularly. Nucleophilic cleav-