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Communications

The Oxidation of (+)-car-3-ene under Gif Type Conditions

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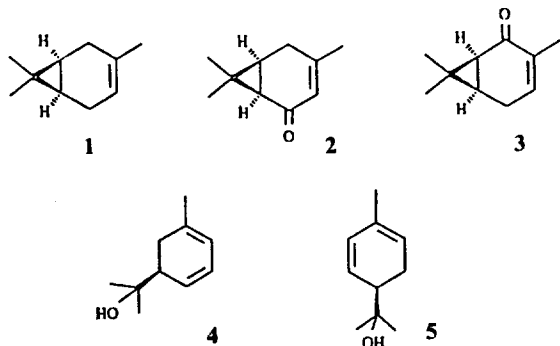
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Extensive studies on the oxidation of (+)-car-3-ene (**1**) by various reagents and oxidative systems have been carried out¹⁻⁵. Most of them show a lack of selectivity for the oxidative process giving rise to complex mixtures of products, some of them with the bicyclo [4.2.0] heptane system rearranged to either an aromatic ring or to an α , β , γ , δ -unsaturated cycloheptadienone. This lack of selectivity has been attributed to the instability of (-)-car-3-en-5-one (**2**) and (+)-car-3-en-2-one (**3**) under acidic or basic conditions^{2,3}.

Our approach to the selective ketonization of saturated hydrocarbon, the Gif system⁶, involves a pyridine-acetic acid solution of the substrate to be oxidized, Zn⁰ as electron source, FeCl₂·4H₂O as catalyst and oxygen (air) as the ultimate



oxidant (Gif IV). Its main characteristics are the oxidation under very mild conditions (room temperature, 1 atm) of saturated hydrocarbons to ketones (with a minimum amount

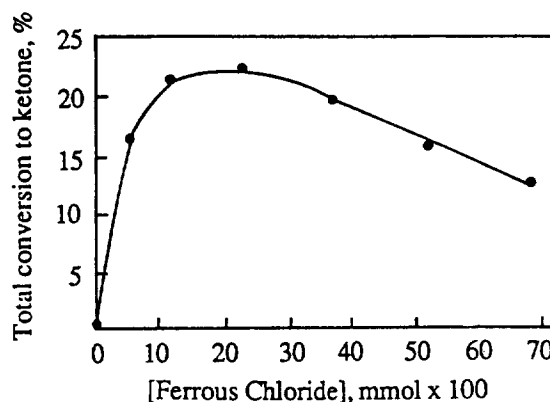


Figure 1. Dependence of the reaction yield on the Fe II concentration⁸.

of alcohol) and the selectivity pattern, sec. > tert. \geq prim., different from that for radical reactions (tert. > sec. > prim.). Cyclic olefins are converted to α , β -unsaturated ketones with or without a double bond shift⁷.

We felt that compound **1** was an interesting substrate to test the mildness of Gif reaction conditions⁸ towards the cyclopropane ring opening⁹ and the rearrangement of the unstable ketones **2** and **3**.

The analysis of the reaction mixture by gas chromatography showed 77% of starting material and the formation of two major compounds. They were isolated by column chromatography and preparative gas chromatography and characterized by comparison with reported⁵ spectroscopic data (¹H-NMR, IR, MS, [α]_D) as ketones **2** and **3** (9% and 6% average isolated yield, respectively). Further elution afforded a new fraction (ca. 7%, average) consisting in a complex mixture of more polar compounds (GC/MS analysis). The mass balance was excellent (99%). An authentic specimen for (+)-car-3-en-2-one was prepared according to a reported procedure¹⁰. These were the only ketones detected, showing that no ring expansion of the bicyclic system had occurred under Gif IV conditions.

We also examined the influence of the Fe II concentration on the conversion of **1** to ketones **2** and **3** (Figure 1). We found that there is an optimum Fe II concentration and addi-

tion of more catalyst decreases the reaction yield. The same behaviour was observed when the oxidation was carried out under GoAgg II conditions¹¹, 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)¹² 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 radicals¹³. 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 μ -oxo-hydroperoxo di-iron intermediate affords an alkyl hydroperoxide, which is then fragmented to the ketone¹⁴. 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**)². These two compounds were found as minor components (<1%) of the polar fraction from the Gif reaction (GC/MS analysis)⁸.

This results confirm the unique mildness and selectivity of Gif chemistry and supports our recently proposed theory¹⁴.

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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 Et_2O and acidified with H_2SO_4 (25%). The aqueous layer was extracted with Et_2O , the organic solutions combined, dried (MgSO_4), and analyzed by gas chromatography. ¹³C-NMR data (at 20 MHz, ppm respect to TMS in 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. H_2O_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 WCl_6 - and MoCl_5 -Based Catalysts

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Various epoxides were polymerized with anionic, cationic, and coordination type catalysts.¹ The polymerization of cyclohexene oxide (CHO) have been carried out by Et_3Al ,² $\text{Al}(\text{acac})_3$ - Ph_3SiOH -alcohol,³ aluminum complex-arylsilyl peroxide,⁴ $\text{Ti}(\text{O}-i\text{-Pr})_4$ - ArOH ,⁵ ZnEt_2 - (1R, 2S) ephedrine,⁶ etc. However there have been no reports on the polymerization of CHO by W- and Mo-based catalysts. WCl_6 - and MoCl_5 -based catalysts exhibited a high catalytic activities on the metathesis polymerization of cycloolefins⁷ and the polymerization of acetylene derivatives.⁸ In recent years we reported the catalytic activities of WCl_6 - and MoCl_5 -based catalysts for the polymerization of acetylene derivatives carrying aromatic heterocycles and the cyclopolymerization of nonconjugated diynes.^{9,10} The present article deals with the studies on the catalytic activity of WCl_6 - and MoCl_5 -based catalysts for the polymerization of CHO.

CHO (Aldrich Chemicals, 98%) was dried with CaH_2 and fractionally distilled. WCl_6 and MoCl_5 (Aldrich Chemicals, re-sublimed, 99+%) were used without further purification.

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.^{9,10}

Table 1 shows the results for the polymerization of CHO by WCl_6 - and MoCl_5 -based catalysts. WCl_6 or MoCl_5 itself shows no catalytic activity. WCl_6 - EtAlCl_2 and MoCl_5 - EtAlCl_2 , which were effective catalysts in the polymerization of some