

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)⁶.

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

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References

1. D. Bakshi, V. K. Mahindroo, R. Soman, and Dev. Sukh, *Tetrahedron*, **45**, 777 (1989).
2. D. A. Baines and W. Cocker, *J. Chem. Soc., Perkin Trans. I*, 2232 (1975).
3. P. H. Boyle, W. Cocker, D. H. Grayson, and P. V. R. Shannon, *J. Chem. Soc. (C)*, 1073 (1971).
4. M. S. Carson, W. Cocker, D. H. Grayson, and P. V. R. Shannon, *Ibid.*, 2220 (1969).
5. W. D. P. Burns, M. S. Carson, W. Cocker, and P. V. R. Shannon, *Ibid.*, 3073 (1968).
6. D. H. R. Barton and N. Ozbalik, in *Activation and Functionalisation of Alkanes*, Ed., Hill, C. L., Wiley, New York, U. S. A., p. 281 (1989).
7. D. H. R. Barton, K. W. Lee, W. Mehl, N. Ozbalik, and L. Zhang, *Tetrahedron*, **46**, 3753 (1990).
8. A solution of (+)-car-3-ene (12.0 mmol) in pyridine (50 ml) containing FeCl₂·4H₂O (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 Et₂O and acidified with H₂SO₄ (25%). The aqueous layer was extracted with Et₂O, the organic solutions combined, dried (MgSO₄), and analyzed by gas chromatography. ¹³C-NMR data (at 20 MHz, ppm respect to TMS in CDCl₃) 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 (M-H₂O⁺), 119, 91.

9. M. Newcomb and A. M. Glenn, *J. Am. Chem. Soc.* **111**, 275 (1989).
10. D. D. Maas, M. Blagg, and D. F. Wiemer, *J. Org. Chem.*, **49**, 853 (1984).
11. A Solution of compound 1 (6.0 mmol) and FeCl₃·6H₂O (0.3 mmol) in pyridine (42.0 ml) was cooled in an ice-water bath. H₂O₂ (30% in water, 2.5 ml, 22.0 mmol) was added dropwise. Reaction samples were worked up as in reference 7.
12. E. About-Jaudet, D. H. R. Barton, E. Csuhai, and N. Ozbalik, *Tetrahedron Lett.*, **31**, 1657 (1990).
13. D. H. R. Barton, E. Csuhai, D. Doller, N. Ozbalik, and G. Balavoine, *Proc. Natl. Acad. Sci. USA*, **87**, 3401 (1990).
14. D. H. R. Barton, E. Csuhai, D. Doller, and G. Balavoine, *J. Chem. Soc., Chem. Commun.*, 1787 (1990).

Synthesis of Poly(cyclohexene oxide) by WCl₆- and MoCl₅-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 Et₃Al,² Al(acac)₃-Ph₃SiOH-alcohol,³ aluminum complex-arylsilyl peroxide,⁴ Ti(O-*i*-Pr)₄-ArOH,⁵ ZnEt₂- (1R, 2S) ephedrine,⁶ etc. However there have been no reports on the polymerization of CHO by W- and Mo-based catalysts. WCl₆- and MoCl₅-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 WCl₆- and MoCl₅-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 WCl₆- and MoCl₅-based catalysts for the polymerization of CHO.

CHO (Aldrich Chemicals, 98%) was dried with CaH₂ and fractionally distilled. WCl₆ and MoCl₅ (Aldrich Chemicals, re-sublimed, 99+%) were used without further purification.

EtAlCl₂ (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 WCl₆- and MoCl₅-based catalysts. WCl₆ or MoCl₅ itself shows no catalytic activity. WCl₆-EtAlCl₂ and MoCl₅-EtAlCl₂, which were effective catalysts in the polymerization of some

Table 1. Polymerization of CHO by WCl₆- and MoCl₅-Based Catalysts^a

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

^aPolymerization was carried out in chlorobenzene for 24 hr. Initial monomer concentration was 2 M. ^bMixture of catalyst and cocatalyst was aged at 30°C for 15 min before use. ^cMole ratio of monomer to catalyst. ^dMethanol-insoluble polymer yield. ^eDetermined by GPC in tetrahydrofuran solution using calibration curve for polystyrene.

acetylene derivatives¹¹ 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. WCl₆-(n-Bu)₄Sn catalyst systems shows no catalytic activities in this polymerization.

IR spectrum of poly (CHO) prepared by WCl₆-EtAlCl₂ catalyst system shows the aliphatic C-H stretching frequency at 2858 and 2935 cm⁻¹ and it shows an absorption band at 1087 cm⁻¹ owing to C-O-C stretching frequency. The ¹H-NMR spectrum of poly (CHO) prepared by WCl₆-EtAlCl₂ 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 WCl₆-EtAlCl₂ and MoCl₅-EtAlCl₂ 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.

References

- (a) S. D. Gagnon, *Encyclopedia of Polym. Sci. & Tech.*, **6**, 225 (1988); (b) M. J. Comstock (ed), "Ring Opening Polymerization, Kinetics, Mechanisms, and Synthesis", 205 (1985).
- R. Bacskai, *J. Polym. Sci.*, A-1, 2777 (1963).
- S. Hayase, T. Ito, S. Suzuki, and M. Wada, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 1433 (1982); (b) S. Hayase, Y. Onishi, K. Yoshikiyo, S. Suzuki, and M. Wada, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 3155 (1982).
- S. Hayase, Y. Onishi, S. Suzuki, and M. Wada, *Macromolecules*, **19**, 968 (1986).
- (a) Y. Fukuchi, T. Takahashi, H. Noguchi, M. Saburi, and Y. Uchida, *J. Polym. Sci. Polym. Lett. Ed.*, **26**, 401 (1988); (b) Y. Fukuchi, T. Takahashi, and Y. Uchida, *Macromolecules*, **20**, 2316 (1987).
- M. Sepulchre, A. Kassamamaly, and N. Spassky, *Polymer*

Preprints, **31**(1), 91 (1990).

- (a) B. A. Dolgoplosk and Yu. V. Korshak, *Russ. Chem. Rev.*, **53**(1), 36 (1984); (b) R. Streck, *CHEMTECH.*, 498 (1989); (c) R. R. Schrock, *Acc. Chem. Res.*, **23**, 158 (1990).
- (a) T. Masuda and T. Higashomura, *Acc. Chem. Res.*, **17**, 51 (1984); (b) S. K. Choi, *The Chemical Fiber*, **71**, 13 (1986).
- (a) Y. S. Gal, H. N. Cho, and S. K. Choi, *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 2021 (1986); (b) Y. S. Gal, H. N. Cho, and S. K. Choi, *Polymer (Korea)*, **14**, 688 (1986); (c) Y. S. Gal, H. N. Cho, S. K. Kwon, and S. K. Choi, *Polymer (Korea)*, **12**, 30 (1988).
- (a) Y. S. Gal and S. K. Choi, *J. Polym. Sci. Polym. Lett. Ed.*, **26**, 115 (1988); (b) Y. H. Kim, Y. S. Gal, U. Y. Kim, and S. K. Choi, *Macromolecules*, **21**, 1991 (1988); (c) M. S. Ryoo, W. C. Lee, and S. K. Choi, *Macromolecules*, **23**, 3029 (1990).
- S. H. Han, Y. S. Gal, S. K. Kwon, and S. K. Choi, *Polymer (Korea)*, **12**, 448 (1988).

A Practical Synthetic Route to Tricyclo [4.3.0.0^{1,5}]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.¹ Acid-mediated ring opening of α -hydroxycyclopropanes provides a route to chain lengthening.² The most versatile chemistry in such transformations of cyclopropyl derivatives certainly stems from cyclopropyl ketones derived from diazoketones and alkenes intramolecularly. Nucleophilic cleav-