Organometallics **1991**, *10*, 807–812

2.10 (t, 3 H, CH_3), 2.12 (d, 2 H, $CH_2CH(CH_3)_2$), 3.42 (q, 2 H, CH_2COOH, J = 0.90 Hz), 12.08 (s br, 2 H, COOH) ppm; ^1H NMR of **5** ($CDCl_3$) δ 0.89 (d, 6 H, $(CH_3)_2CH$), 1.86 (t, 3 H, CH_3), 1.87 (m, 1 H, $CH(CH_3)_2$), 2.56 (d, 2 H, $CH_2CH(CH_3)_2$), 3.39 (q, 2 H, CH_2COOH, J = 0.56 Hz), 12.15 (s br, 2 H, COOH) ppm; ^{13}C NMR of **4** ($CDCl_3$) δ 21.1, 22.1 (methyl carbons), 26.7 ($CH_2CH(CH_3)_2$), 35.2 (CH_2COOH), 44.7 ($CH(CH_3)_2$), 123.0, 148.8 (olefinic carbons), 169.3, 172.9 (COOH) ppm; ^{13}C NMR of **5** ($CDCl_3$) δ 20.8, 22.3 (methyl carbons), 26.9 ($CH_2CH(CH_3)_2$), 35.5 (CH_2COOH), 43.6 ($CH(CH_3)_2$), 123.1, 149.4 (olefinic carbons), 169.4, 172.6 (COOH) ppm; MS (*m/e*) 182, $[M - H_2O]^+$; mp 169.5–169.8 °C.

4/**5** (R = Ph): IR (ν_{CO}) 1710, 1665 cm^{-1}; ^1H NMR of **4** ($CDCl_3$) δ 2.40 (t, 3 H, CH_3), 3.16 (q, 2 H, CH_2, J = 0.93 Hz), 7.31 (m, 5 H, Ph), 12.37 (s br, 2 H, COOH) ppm; ^1H NMR of **5** ($CDCl_3$) δ 2.13 (t, 3 H, CH_3), 3.53 (q, 2 H, CH_2, J = 0.60 Hz), 7.30 (m, 5 H, Ph), 12.33 (s br, 2 H, COOH); ^{13}C NMR ($CDCl_3$) δ 23.1 (CH_3), 36.9 (CH_2), 123.7, 126.8, 127.7, 128.7, 143.2, 149.5 (olefinic and aromatic carbons), 169.2, 172.8 (COOH) ppm; MS (*m/e*) 202, $[M - H_2O]^+$; mp 149.4–150.8 °C.

Acknowledgment. We are grateful to British Petroleum and to the Natural Sciences and Engineering Research Council of Canada for support of this research. We are indebted to Prof. G. W. Gokel for a valuable discussion and suggestions.

Opening of Oxirane Rings by the Conjugate Base of Pentacarbonyl(methoxymethylcarbene)chromium in the Presence of Boron Trifluoride Etherate: A General and Improved Synthesis of Pentacarbonyl(2-oxacyclopentylidene)chromium Compounds

Luciano Lattuada, Emanuela Licandro,* Stefano Maiorana,* Henriette Molinari, and Antonio Papagni

Dipartimento di Chimica Organica e Industriale dell'Università, Via Venezian 21, I-20133 Milano, Italy

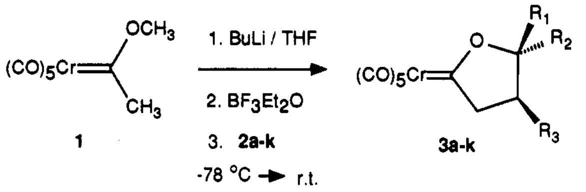
Received March 16, 1990

A modified procedure for the synthesis of new pentacarbonyl(2-oxacyclopentylidene)chromium compounds is reported. Its application to optically pure epoxides allowed us to obtain the corresponding optically pure cyclic chromium carbene complexes. The oxidation of the (2-oxacyclopentylidene)pentacarbonylchromium compounds led to the corresponding substituted γ-butyrolactones.

Introduction

Pentacarbonyl(alkoxyalkylcarbene)chromium complexes are well-known, useful substrates in organic synthesis.[1] Structural features unique to this type of compound, i.e., the presence of a pentacarbonylchromium residue and a carbon–chromium double bond, modulate the chemistry of these organometallics. The fact that the carbon–metal double bond can be easily cleaved under mild oxidative conditions and transformed into a carbonyl group gives additional versatility to these compounds. Thus, these complexes are already routinely employed as synthetic precursors of various derivatives of chemical and biological significance, such as β-lactams,[2] indole alkaloids,[3] cyclobutanones,[4] and anthracyclinone synthons.[5] For these reasons, the research in this area has been directed toward the synthesis of new complexed carbenes and their utilization as substrates for preparing useful derivatives.

Scheme I



In particular, one class of these derivatives, the pentacarbonyl(2-oxacyclopentylidene) chromium complexes, although very promising, has enjoyed little popularity in organic synthesis up to now. In 1974, Casey reported[6] the first synthesis of four pentacarbonyl(2-oxacyclopentylidene)chromium complexes obtained from the reaction of pentacarbonyl(methoxymethylcarbene)chromium and pentacarbonyl(ethylmethoxycarbene)chromium complexes with ethylene and propylene oxides. More recently, Doetz published[7] a new synthetic procedure for one of these compounds, the unsubstituted pentacarbonyl(2-oxacyclopentylidene)chromium, starting from $(CO)_5Cr{\cdot}OEt_2$ and 1-butyn-4-ol. Little data[8] are available on the chemical reactivity of these carbene derivatives, and their synthetic usefulness has yet to be fully exploited. Moreover, the synthetic procedure reported by Casey proved not to be

---

(1) Review: (a) Doetz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1984. (b) Doetz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(2) Borel, C.; Hegedus, L. S.; Krebs, J.; Satoh, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1101.

(3) Bauta, W. E.; Wulff, W. D.; Pavkovic, S. F.; Zaluzec, E. J. *J. Org. Chem.* **1989**, *54*, 3249.

(4) Sierra, M. A.; Hegedus, L. S. *J. Am. Chem. Soc.* **1989**, *111*, 2335.

(5) Doetz, K. H.; Popall, M.; Müller, G.; Ackermann, K. *J. Organomet. Chem.* **1990**, *383*, 93.

(6) Casey, C. P.; Anderson, R. L. *J. Organomet. Chem.* **1974**, *73*, C28–C30.

(7) Doetz, K. H.; Sturm, W.; Alt, H. G. *Organometallics* **1987**, *6*, 1424. See also: Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1986**, 514.

(8) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1975**, *102*, 175.

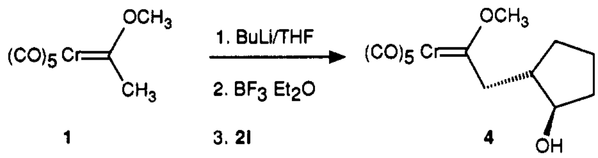
0276-7333/91/2310-0807$02.50/0

Table I. Reaction Yields and Physical and Analytical Data for Compounds 3b–k,p, 4, and 8

complex	yield, %	mp, °C^a	mol formula	*m/z*	anal. found (calcd) C	H
3b	65	oil	$C_{11}H_{10}CrO_6$	290	45.8 (45.52)	3.5 (3.45)
3c	45	62–63	$C_{10}H_7ClCrO_6$	310	38.81 (38.67)	2.32 (2.27)
3d	38	59–60	$C_{10}H_7BrCrO_6$	354	34.03 (33.82)	2.07 (1.99)
3e	32	33	$C_{14}H_{12}CrO_8$	360	47.08 (46.67)	3.45 (3.36)
3f	68	74	$C_{15}H_{10}CrO_6$	338	53.43 (53.26)	2.97 (2.98)
3g	48	97–98	$C_{13}H_{12}CrO_6$	316	49.55 (49.37)	3.79 (3.82)
3h	25	106–107	$C_{14}H_{14}CrO_6$	330	51.05 (50.91)	4.20 (4.27)
3i	53	36	$C_{11}H_{10}CrO_6$	290	45.37 (45.52)	3.55 (3.47)
3j	18	74–76	$C_{14}H_{14}CrO_6$	330	51.07 (50.91)	4.17 (4.27)
3k	5	93–94	$C_{21}H_{14}CrO_6$	414	60.92 (60.87)	3.4 (3.38)
3p	40	103–105 dec	$C_{17}H_{11}CrNO_{10}$	441	46.4 (46.26)	2.52 (2.49)
4	30	57–58	$C_{13}H_{14}CrO_7$	334	46.94 (46.71)	4.31 (4.22)
8	25	59–60	$C_{11}H_8CrO_6$	288	46.06 (45.9)	2.8 (2.7)

^{a} All solid products were crystallized from pentane at −78 °C.

Scheme II



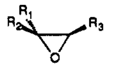
1 **4**

of general applicability: in our hands the reaction of epoxides **2c–g** yielded the corresponding derivatives **3c–g** in unsatisfactory yields.

In our opinion these compounds have great potential in organic synthesis as precursors of γ-butyrolactones and useful intermediates easily susceptible to further functionalization, particularly in the position α with respect to the carbene carbon atom. Prompted by this interest, we have developed a general and simple synthetic procedure for the preparation of a series of variously substituted pentacarbonyl(2-oxacyclopentylidene)chromium complexes.

Results and Discussion

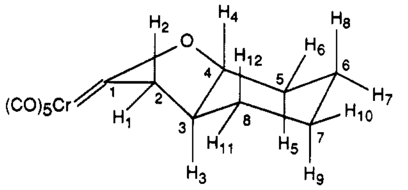
We have modified[9] the original Casey procedure, substituting tetrahydrofuran for diethyl ether as the solvent and adding $BF_3{\cdot}Et_2O$ as an activating agent;[10] under these new conditions complex **1**, in reaction with epoxides **2a–k**, afforded substituted pentacarbonyl(2-oxacyclopentylidene)chromium complexes **3a–k** in good yields (Scheme I).



2a-m

	R_1	R_2	R_3		R_1	R_2	R_3
a:	CH_3	H	H	h:	H	-$(CH_2)_5$-	
b:	C_2H_5	H	H	i:	H	CH_3	CH_3
c:	CH_2Cl	H	H	j:	-$(CH_2)_5$-		H
d:	CH_2Br	H	H	k:	H	C_6H_5	C_6H_5
e:	$CH_2OCOC(CH_3)$=CH_2	H	H	l:	H	-$(CH_2)_3$-	
f:	H	H	C_6H_5	m:	CH_3	CH_3	OCH_3
g:	H	-$(CH_2)_4$-					

Compound **3a** has been previously characterized;[6] reaction yields and physical and analytical data of compounds **3b–k** are listed in Table I and spectroscopic data in Tables II–IV.[11] According to the mechanism proposed by Casey, the reaction is stereospecific and the cis epoxides **2g,h,i,k** yield the corresponding trans-3,4-disubstituted derivatives **3g,h,i,k** as the only stereoisomers. As expected, the oxirane rings undergo attack at the less substituted carbon atom, with the only exception being styrene oxide **2f**; in this case, in the presence of $BF_3{\cdot}Et_2O$, the only isolated product is pentacarbonyl(4-phenyl-2-oxacyclopentylidene)chromium (**3f**), arising from attack on the more substituted carbon atom of the epoxide, whereas in the absence of $BF_3{\cdot}Et_2O$ a 60:40 mixture of the 3-phenyl and 4-phenyl regioisomers is obtained.[12] The reaction of carbene **1** with cyclopentene oxide **2l** afforded the open-chain compound **4** (Scheme II); this outcome may be rationalized by considering that the bicyclic system of the expected product, containing two five-membered rings, is not compatible with a trans junction. Physical and analytical data for compound **4** are reported in Table I and spectroscopic data in Tables II and III. NMR analysis of the bicyclic carbene **3g**, arising from reaction of compound **1** with cyclohexene oxide **2g**, allowed us to establish the correct stereochemistry of the ring junction. A ^{13}C DEPT experiment led to the assignment of the two unique methine carbons in compound **3g** (Figure 1), one at 98.6 ppm, adjacent to the oxygen (C4), and the other at 43.4 ppm (C3). The methylene carbon (C2), adjacent to the chromium–carbon double bond, appears at 65.3 ppm. A 2D ^{13}C–^1H heterocorrelated experiment was then performed: this was the key step for the assignment of the hydrogens at the junction of the two cycles. The two hydrogens H4 and H3 (Figure 1), correlated with two methine carbons, occur at 3.95 and 1.45 ppm, respectively. This assignment was not straightforward on the basis of the ^1H–^1H homocorrelated map, due to the extensive pattern of coupling and overlapping in the region 1–2 ppm. By combining the information from the ^{13}C–^1H heterocorrelated map and the 2QF COSY experiment, it was possible to complete the assignment of the ^{13}C–^1H spec-



3g

Figure 1.

---

[9] Preliminary results have been published in: *NATO ASI Ser., Ser. C* **1989**, *269*, 149.

[10] The only example of the use of a Lewis acid as activating agent in the reaction of pentacarbonylchromium carbenes with electrophiles has been reported by: Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503.

[11] Only selected examples of ^{13}C NMR spectra are reported.

[12] It was already reported that the opening of styrene oxide with carbanions in alkaline medium afforded a mixture of both regioisomers: Smith, J. G. *Synthesis* **1984**, 629.

Table II. ^1H NMR Data for Compounds 3b–k,p, 4, and 8

compd	^1H NMR δ, ppm
3b	1.1 (t, 3 H, CH_3, J_{vic} = 7.5 Hz); 1.35–2.20 (m, 4 H, CH_2 + CH_2CH_3); 3.68 (ddd, 1 H, CH—C=Cr, J_{gem} = 20.2 Hz, J'_{vic} = 8.5 Hz, J''_{vic} = 7.5 Hz); 4.05 (ddd, 1 H, CH—C=Cr, J_{gem} = 20.2 Hz, J'_{vic} = 9 Hz, J''_{vic} = 5 Hz); 5.0 (m, 1 H, CH—O)
3c	1.78–2.20 (m, 2 H, CH_2); 3.62 (ddd, 1 H, CH—C=Cr, J_{gem} = 20 Hz, J'_{vic} = 10 Hz, J''_{vic} = 6 Hz); 3.78 (dd, 1 H, CHCl, J_{gem} = 12 Hz, J_{vic} = 4 Hz); 3.91 (ddd, 1 H, CH—C=Cr, J_{gem} = 20 Hz, J'_{vic} = 10 Hz, J''_{vic} = 6 Hz); 4.02 (dd, 1 H, CHCl, J_{gem} = 12 Hz, J_{vic} = 4 Hz); 5.47 (m, 1 H, CH-O)
3d	1.77–2.21 (m, 2 H, CH_2); 3.61 (ddd, 1 H, CH—C=Cr, J_{gem} = 24 Hz, J'_{vic} = 10.5 Hz, J''_{vic} = 6.9 Hz); 3.69 (dd, 1 H, CH—Br, J_{gem} = 11.4 Hz, J_{vic} = 3.3 Hz); 3.85 (dd, 1 H, CH—Br, J_{gem} = 11.4 Hz, J_{vic} = 4.8 Hz); 3.95 (ddd, 1 H, CH—C=Cr, J_{gem} = 24 Hz, J'_{vic} = 9.9 Hz, J''_{vic} = 5.4 Hz); 5.44 (m, 1 H, CH—O)
3e	1.9 (s, 3 H, CH_3); 1.7–2.2 (m, 2 H, CH_2); 3.63 (ddd, 1 H, CH—C=Cr, J_{gem} = 21.5 Hz, J'_{vic} = 10 Hz, J''_{vic} = 7.5 Hz); 3.82 (ddd, 1 H, CH—C=Cr, J_{gem} = 21.5 Hz, J'_{vic} = 10 Hz, J''_{vic} = 6.2 Hz); 1.37 (dd, 1 H, CH—O—CO, J_{gem} = 12.5 Hz, J_{vic} = 5 Hz); 4.63 (dd, 1 H, CH—OCO, J_{gem} = 12.5 Hz, J_{vic} 3.8 Hz); 5.4 (m, 1 H, CH—O); 5.62 (m, 1 H, $(CH_3)CH=CH_2$); 6.1 (s, 1 H, $(CH_3)CH=CH_2$)
3f	3.3–3.7 (m, 1 H, CH); 3.75 (dd, 1 H, CH—C=Cr, J_{gem} = 21.7 Hz, J_{vic} = 5.3 Hz); 4.01 (dd, 1 H, CH—C=Cr, J_{gem} = 21.7 Hz, J_{vic} = 8 Hz); 4.89 (dd, 1 H, CH—O, J_{gem} = 18.3 Hz, J_{vic} = 5.7 Hz); 5.2 (dd, 1 H, CH—O, J_{gem} = 18.3 Hz, J_{vic} = 8 Hz); 6.9–7.5 (m, 5 H, Ph)
3g	1.4 (m, 1 H, H_8); 1.45 (m, 1 H, H_3); 1.5 (m, 1 H, H_6); 1.6 (m, 1 H, H_9); 1.8 (m, 2 H, H_7, H_{11}); 2.45 (m, 1 H, H_5), 2.5 (m, 1 H, H_2); 3.9 (m, 1 H, H_4); 4.0 (m, 1 H, H_1)
3h	1.15–2.1 (m, 10 H, $(CH_2)_5$); 2.7 (m, 1 H, $CH—CH_2—C=Cr$); 2.78 (dd, 1 H, CH—C=Cr, J_{gem} = 19.6 Hz, J_{vic} = 11.4 Hz); 4.18 (dd, 1 H, CH—C=Cr, J_{gem} = 19.6 Hz, J_{vic} = 6.8 Hz); 4.6 (m, 1 H, CH—O)
3i	1.04 (d, 3 H, $CH_3—CH—O$); 1.54 (d, 3 H, $CH_3—CH$); 1.87 (m, 1 H, $CH—CH_3$); 3.06 (dd, CH—C=Cr, J_{gem} = 19.7 Hz, J_{vic} = 8.4 Hz); 3.96 (dd, 1 H, CH—C=Cr, J_{gem} = 19.7 Hz, J_{vic} = 7.5 Hz); 4.66 (m, 1 H, CH—O)
3j	1.4–2.3 (m, 12 H, $(CH_2)_5$, $CH_2—CH_2—C=Cr$); 3.60 (d, 1 H, CH—Cr, J_{gem} = 8 Hz); 3.65 (d, 1 H, CH—C=Cr, J_{gem} = 8 Hz)
3k	3.41 (m, 1 H, Ph—CH—CH_2, $^3J_{vic}$ = 8 Hz); 3.72 (dd, 1 H, CH—C=Cr, J_{gem} = 20.5 Hz, J_{vic} = 8 Hz); 4.37 (dd, 1 H, CH—C=Cr, J_{gem} = 20.5 Hz, J_{vic} = 8 Hz), 5.98 (d, 1 H, J_{vic} = 8 Hz)
3p	1.7–1.9 (m, 2 H, $CH_2—CH—O$); 3.64 (ddd, 1 H, CH—C=Cr, J_{gem} = 21 Hz, J'_{vic} = 12 Hz, J''_{vic} = 7.5 Hz); 3.89 (ddd, 1 H, CH—C=Cr, J_{gem} = 21 Hz, J'_{vic} = 11.2 Hz, J''_{vic} = 6 Hz); 4.58 (dd, 1 H, CH—OCO, J_{gem} = 12.7 Hz); 4.85 (dd, 1 H, CH—OCO, J_{gem} = 12.7 Hz, J_{vic} = 3 Hz); 5.4–5.6 (m, 1 H, CH—O); 8.1–8.5 (m, 4 H, Ph)
4	1.39 (d, 1 H, OH); 1.1–2.2 (m, 6 H, 3 CH_2–); 2.15 (m, 1 H, $CH—CH_2—C=Cr$, $^3J_{vic}$ = 8 Hz); 3.34 (dd, 1 H, CH—C=Cr, J_{gem} = 16 Hz, J_{vic} = 8 Hz); 3.51 (dd, 1 H, CH—C=Cr, J_{gem} = 16 Hz, J_{vic} = 6 Hz); 3.77 (m, 1 H, CH—OH, $^2J_{vic}$ = 8 Hz, $J_{CH—OH}$ = 6 Hz); 4.70 (s, 3 H, OCH_3)
8[a]	1.6 (s, 6 H, 2 CH_3); 7.1 (2 d, 2 H, CH=CH, J_{vic} = 4.5 Hz)

[a] ^1H NMR spectrum recorded in CCl_4.

trum (^1H (ppm): H1, 4.1; H4, 3.95; H2, 2.6; H5, 2.5; H7, 1.9; H11, 1.9; H9, 1.7; H6, 1.6; H3, 1.45; H8, 1.3; H12, 1.2; H10, 1.1). The proton chemical shifts were determined with a ^1H–^1H J-resolved experiment. The fusion of the system is trans, as revealed from the pattern of coupling constants of H4 with the adjacent hydrogens: J = 11.5, 11.5, 3.86 Hz, corresponding to two anti-periplanar and one gauche arrangement, as expected for a trans fusion. The 11.5-Hz value of the coupling constant between H4 and H3 was confirmed from the analysis of the second-order system H3.

Table III. IR Spectral Data for Complexes 3b–k, 4, and 8

complex	ν, cm^{-1} (Nujol)
3b[a]	2070, 2000, 1950 (broad)
3c	2060, 1970, 1920 (broad)
3d	2060, 1970, 1920 (broad)
3e	2050, 1980, 1930 (broad), 1700, 1620
3f	2060, 1970, 1940 (broad)
3g	2040, 1990, 1930 (broad)
3h	2060, 2000 (broad)
3i	2060, 1980, 1950 (broad)
3j	2060, 1950 (broad)
3k	3030, 2060, 1985, 1950 (broad), 1600
4	3340, 2040, 1950 (broad)
8	2060, 1990, 1950 (broad), 1560

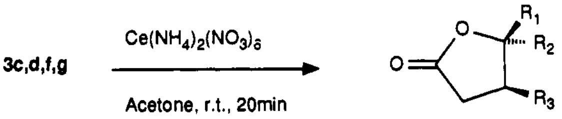
[a] Neat liquid.

Table IV. ^{13}C NMR Data[a] for Complexes 3g–i,n,o and 8

		$C_{M—CO}$		
complex	$C_{carbene}$	trans	cis	all other C atoms
3g	342.80	223.60	216.50	24.23, 25.29, 27.9, 30.19, 43.44, 65.36, 98.66
3h	342.85	223.64	216.51	24.8, 24.95, 28.21, 28.44, 31.73, 41.65, 68.62, 101.7
3i	342.15	223.73	216.46	16.28, 19.01, 37.08, 68.74, 100.57
3n	340.17	223.58	216.39	20.5, 28.13, 60.89, 95.87
3o	342.52	223.31	216.33	40.9, 68.57, 90.85, 126.3, 126.48, 127.57, 128.99, 129.17
8	320.24	224.53	216.58	24.50, 106.84, 139.45, 154.58

[a] Shifts in ppm; internal reference $CDCl_3$; $CDCl_3$ solutions.

Scheme III



6a-d

complex	R_1	R_2	R_3	yield %
6a	CH_2Cl	H	H	30
6b	CH_2Br	H	H	70
6c	H	H	Ph	65
6d	H	- $(CH_2)_4$ -		65

Some of the new carbene complexes reported in Scheme I were oxidized to the corresponding γ-butyrolactones; thus, complexes **3c,d,f,g** treated with $Ce(NH_4)_2(NO_3)_6$, as already described for other Fischer type carbene complexes,[8] gave products **6a–d** (Scheme III).[13]

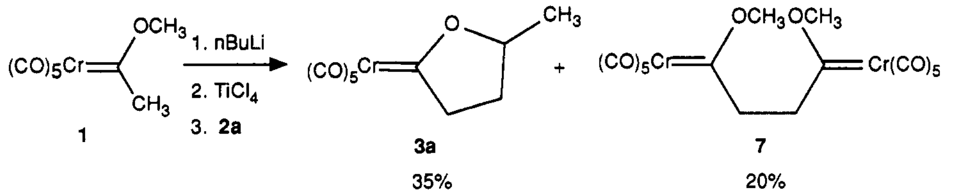
We were also interested in proving whether other Lewis acids could be as effective as $BF_3·Et_2O$ in assisting the opening of oxirane rings; thus, we selected $TiCl_4$ because it was successfully employed by Wulff.[10] However, in the reaction of the anion of carbene **1** with propylene oxide **2a** in the presence of $TiCl_4$, the yield in product **3a** was as low as 35%, and another product, the dimeric carbene **7**, was also formed in 20% yield. Probably, in this case, the carbanion of carbene **1** is oxidized by Ti(IV)[14] to a radical species that undergoes dimerization to the carbene **7** (Scheme IV). On the basis of this unexpected result,

---

[13] Compounds **6a–d** have been previously synthesized by different routes. **6a**: Damin, B.; Forestiere, A.; Garapon, J.; Sillion, B. *J. Org. Chem.* **1981**, *46*, 3552. **6b**: *Beilstein Handbook of Organic Chemistry*; Springer-Verlag: Berlin, 1933; Vol. 17, p 236. **6c**: see ref 12. **6d**: Pirke, W. H.; Adams, P. E. *J. Org. Chem.* **1980**, *45*, 4111.

[14] Ojima, I.; Inaba, S. *Tetrahedron Lett.* **1977**, *23*, 2009.

Scheme IV



Scheme V

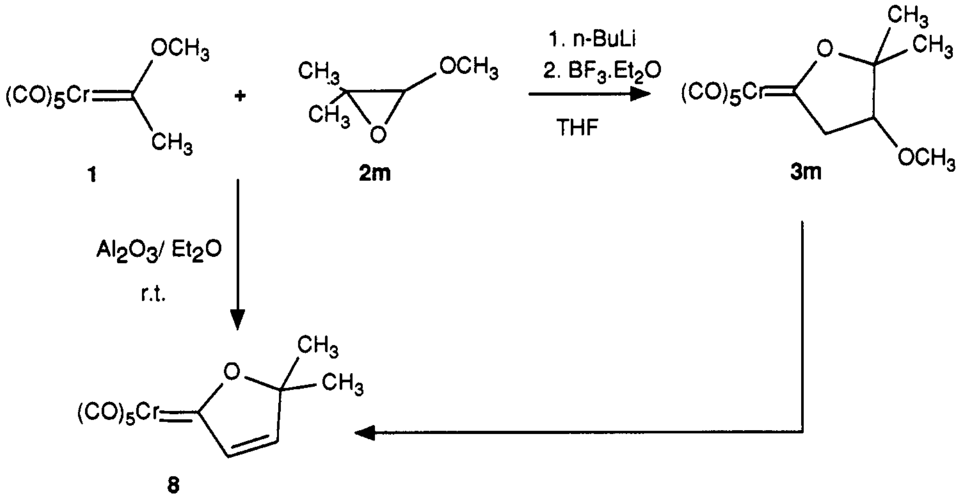
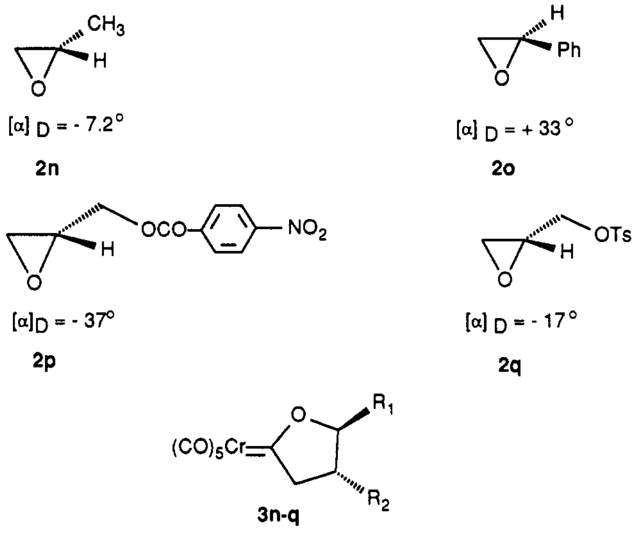


Chart I



	R$_1$	R$_2$	yield%	[α]$_D$
n	CH$_3$	H	72.6%	- 19.8°
o	H	Ph	43.9%	+156.3°
p	CH$_2$OCO-C$_6$H$_4$-pNO$_2$	H	34.6%	+ 76.1°
q	CH$_2$OTs	H	6.9%	+ 45.9°

we attempted to maximize the formation of product 7 in this reaction, which would then represent a convenient synthetic procedure leading to dimeric carbenes; accordingly, the reaction of carbene 1 and TiCl$_4$ was run without epoxide. However, even under these conditions, the yield in product 7 could not be improved.

Under the same reaction conditions described in Scheme I, the commercially available epoxy ether **2m** with the conjugate base of carbene 1 yielded pentacarbonyl(4-methoxy-3,3-dimethyl-2-oxacyclopentylidene)chromium (**3m**). This product is quite unstable and could not be fully characterized; in fact, partial loss of one molecule of methanol occurs even during workup, yielding the α,β-unsaturated cyclic carbene 8 (Scheme V). Compound 8 is the only isolable reaction product when carbene 1 and epoxide **2m** are allowed to react in diethyl ether and in the presence of neutral alumina at room temperature,[15] without preforming the carbanion of 1. Physical and analytical data for compound 8 are reported in Table I and spectroscopic data in Tables II–IV. It is worthy of note that complexes 8 and **3j** represent the first examples of Fischer type carbene complexes having a tertiary carbon atom directly attached to the oxygen.

A recent synthetic procedure[16] allows easy access to epoxy ethers bearing electron-withdrawing substituents; taking advantage of this possibility, we are planning to extend the study carried out with epoxy ether **2m** to these newly available substrates in reactions with chromium carbene conjugate bases.

With the aim of synthesizing optically active pentacarbonyl(2-oxacyclopentylidene)chromium, from which the corresponding optically active γ-butyrolactones can be prepared, we have carried out the reaction described in Scheme I on commercially available optically pure epoxides **2n–q**. The reactions of these compounds with the conjugate base of carbene 1 were completely stereospecific, leading to exclusive formation of the optically active carbene complexes **3n–q** (Chart I). The optical purity of compounds **3n–p** was based on the $[\alpha]_D$ values of the corresponding lactones **9n–p**, obtained from **3n–p** by oxidation.[17] Thus, solutions of compounds **3n,p** in diethyl ether were exposed to air and sunlight, while carbene **3o**

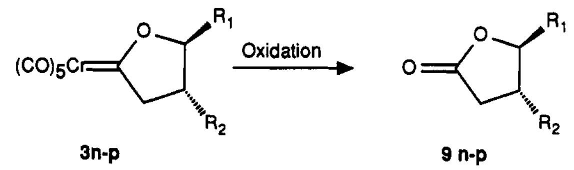
---

(15) Rudler-Chauvin, M.; Rudler, H. *J. Organomet. Chem.* **1981**, *212*, 203.

(16) Giumanini, A. G.; Strazzolini, P.; Verardo, G. *J. Org. Chem.* **1988**, *53*, 332.

(17) Because of the low yield of compound **3q**, we have not oxidized it to the corresponding γ-butyrolactone.

Scheme VI[a]

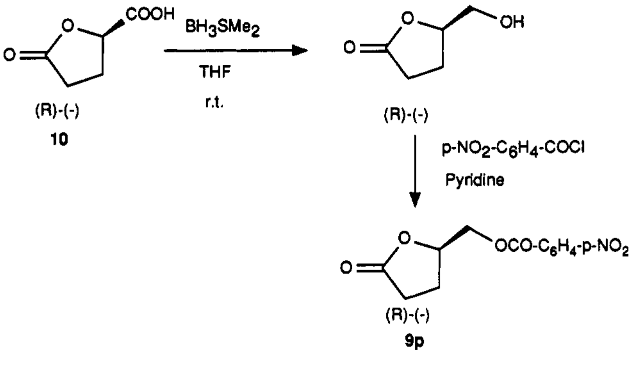


3n-p → 9 n-p

	R_1	R_2	yield %	$[\alpha]_D$
n:	Me	H	71	-31.9°
o:	H	Ph	79	+50.9°
p:	$CH_2OCO\text{-}C_6H_4\text{-}pNO_2$	H	84	-44.1°

[a] Oxidation conditions: for **3n,p**, $O_2/h\nu/Et_2O$; for **3o**, pyN—O/CH_2Cl_2.

Scheme VII



43%, $[\alpha]_D = -45.4°$

was treated with pyridine oxide: the lactones **9n** and **9o** had the same $[\alpha]_D$ values as the ones reported[18] (Scheme VI); the unknown optically active lactone **9p** showed the same $[\alpha]_D$ value as the one we synthesized by reducing (R)-(−)-5-oxo-2-tetrahydrofurancarboxylic acid (**10**) to the corresponding alcohol with $BH_3{\cdot}SMe_2$[19] and making the ester with *p*-nitrobenzoyl chloride in pyridine solution (Scheme VII).

In summary, the study reported in this article represents a general synthetic procedure for (3,4-disubstituted-2-oxacyclopentylidene)chromium complexes of defined stereochemistry; moreover, this method yields optically pure derivatives. Since the above complexes are easily oxidized, the entire procedure can also be regarded as a new method for preparing substituted γ-butyrolactones; as an example of this application, we are currently studying the synthesis of a naturally occurring trans-3,4-disubstituted γ-butyrolactone, (±)-eldanolide.[20] Finally, complexes **3** represent new pentacarbonylchromium carbenes available for subsequent transformation, particularly in the α-position; work in progress in our laboratories is addressing this promising aspect of carbene chemistry.

Experimental Section

General Comments. All melting points were obtained with a Büchi apparatus and are uncorrected. Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian EM 390 (90 MHz), XL 200 (200 MHz), Bruker WP 80 ST (80 MHz); ^{13}C NMR, Varian XL 200, 300 (200, 300 MHz). Chemical shifts are reported in δ (Me_4Si as internal standard with Varian EM 390 instrument, $CDCl_3$ in all other cases). IR spectra were recorded on a Perkin-Elmer 298 spectrometer. Mass spectra were taken with a Varian MAT 311-A spectrometer equipped with a combined EI–FI–FD ion source. Optical rotations were measured on a Perkin-Elmer 241 polarimeter using a sodium lamp. All chromatographic isolations were accomplished by flash column chromatography, with silica gel 60 (230–400 mesh). All samples were filtered on Millex-SR 0.5-μm filters (Millipore Waters), before NMR measurements.

Materials. Tetrahydrofuran and diethyl ether used for the reactions were freshly distilled over sodium–lead alloy (Fluka) with benzophenone under an argon atmosphere just before use. Petroleum ether (bp 30–60 °C) was used for chromatographic purifications. Pentacarbonyl(methylmethoxycarbene)chromium(0) (**1**) was synthesized according to a literature procedure.[21] $BF_3{\cdot}Et_2O$, purchased from Fluka, was distilled over CaH_2 at atmospheric pressure.

General Procedure for the Synthesis of Pentacarbonyl(2-oxacyclopentylidene)chromium(0) Compounds 3a–k,n–q and of Compound 4. To a tetrahydrofuran solution of the conjugate base of pentacarbonyl(methoxymethylcarbene)chromium(0) (from 6 mmol of **1** and 7.2 mmol of 10 M *n*-BuLi in *n*-hexane at −78 °C for 30 min and then 30 min at −20 °C) was added freshly distilled $BF_3{\cdot}Et_2O$ (6.6 mmol) with a syringe at −78 °C, under an argon atmosphere, followed after 10 min by a tetrahydrofuran solution of epoxides **2a–e,n–q** (6.6 mmol). The mixture was allowed to react at −78 °C for 1 h and then at −20 °C until disappearance of the starting carbene (4–24 h). The reaction mixture, brought to room temperature, was diluted with water, extracted with diethyl ether, and dried over Na_2SO_4. The pentacarbonyl(2-oxacyclopentylidene)chromium complexes **3a–k,n–q** and compound **4** were recovered, from the crude reaction mixture, by flash column chromatography. Eluent used were as follows: compounds **3i,h,g,j**, *n*-pentane; **3k**, *n*-pentane/CH_2Cl_2 (7:3); **3f,e,o**, **4**, petroleum ether/diethyl ether (7:3); **3c,d**, petroleum ether/diethyl ether (8:2); **3b**, *n*-pentane/CH_2Cl_2 (9:1); **3n**, *n*-hexane/CH_2Cl_2 (9.5:0.5); **3p,q**, petroleum ether/diethyl ether (1:1).

Oxidation of Complexes 3c,d,f,g to Lactones 6a–d. To a solution of complexes **3c,d,f,g** (2.2 mmol) in 40 mL of acetone was added ceric ammonium nitrate (6.6 mmol) at room temperature. After 30 min the solvent was evaporated under reduced pressure and the residue taken up with water (200 mL) and extracted with diethyl ether (100 mL). The organic layer was separated and dried over Na_2SO_4; after filtration and evaporation of the solvent the residue was purified by flash column chromatography (eluent petroleum ether/diethyl ether (1:1)). Yields of lactones **6a–d** are reported in Scheme III.

Reaction of Compound 1 with Propylene Oxide and $TiCl_4$. To a tetrahydrofuran solution of the conjugate base of pentacarbonyl(methoxymethylcarbene)chromium(0) (from 2 mmol of **1** and 2.2 mmol of 1.6 M *n*-BuLi in *n*-hexane at −78 °C for 30 min) were added $TiCl_4$ (2 mmol) and propylene oxide (**2a**; 2 mmol) at −78 °C. The mixture was allowed to react for 20 h at −20 °C. Water (100 mL) was then added, and the resulting suspension was extracted with diethyl ether (150 mL). After separation, the organic layer was dried over Na_2SO_4, filtered over Celite, and evaporated under reduced pressure. The residue was purified by flash column chromatography with *n*-pentane. Three fractions were recovered: unreacted **1** (13%), pentacarbonyl(3-methyl-2-oxacyclopentylidene)chromium(0) (**3a**, 35%), and carbene complex **7** (20%). Data for **7**: yellow crystals, mp 93 °C (pentane −78 °C); ^1H NMR ($CDCl_3$) δ 3.6 (s, 4 H, CH_2CH_2), 4.7 (s, 6 H, OCH_3). Anal. Calcd for $C_{16}H_{10}Cr_2O_{12}$: C, 38.56; H, 2.02; Found: C, 38.38; H, 2.01.

Reaction of Carbene 1 with 3-Methoxy-2-methyl-2,3-epoxypropane (2m) in the Presence of Alumina: Synthesis of Compound 8. To a solution of complex **1** (4.15 mmol) in 30 mL of anhydrous diethyl ether were added 25 g of neutral alumina and epoxide **2m** (63 mmol) at room temperature, under an argon atmosphere. After 5 h the solvent was evaporated under reduced pressure and the residue purified by flash column chromatography

---

(18) (a) Lawston, I. W.; Inch, T. D. *J. Chem. Soc., Perkin Trans. 1*, **1983**, 2629. (b) Barbier, P.; Benezra, C. *J. Med. Chem.* **1982**, *25*, 943.

(19) Silverstein, R. M.; Ravid, U.; Smith, L. R. *Tetrahedron* **1978**, *34*, 1449.

(20) Kunesch, G.; Zagatti, P. *Tetrahedron* **1981**, *22*(52), 5271.

(21) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954.

(eluent petroleum ether/diethyl ether (8:2)).

Two fractions were recovered: unreacted compound 1 (51%) and compound 8 (25%, red crystals). Analytical and spectroscopic data are reported in Tables I-IV.

Oxidation of Carbenes 3n,p to Lactones 9n,p. A solution of carbene **3n** (3.63 mmol) in 70 mL of diethyl ether was irradiated with sunlight under a slight air flow. After 36 h, the reaction mixture was filtered over Celite and the solvent was evaporated under reduced pressure. Compound **9n**: oil, yield 71%; $[\alpha]_D = -31.9°$ (T = 65%; c = 0.908, CH_2Cl_2) (lit.[18b] $[\alpha]_D = -29.6°$ (c = 1.29, CH_2Cl_2)).

A similar procedure for carbene **3p** gave a crude reaction mixture, from which recrystallization from benzene/*n*-hexane gave product **9p**: mp 145-147 °C (84%); $[\alpha]_D = -44.1°$ (T = 65%; c = 0.39, $CHCl_3$).

Oxidation of Carbene 3o to Lactone 9o. To a solution of carbene **3o** (0.68 mmol) in 8 mL of dichloromethane was added 1.36 mmol of pyridine oxide in 3 mL of dichloromethane; the mixture was allowed to react at room temperature, with magnetic stirring, for 3 h. The solvent was evaporated, the residue was taken up with diethyl ether (100 mL), and the solution was washed with 80 mL of 10% HCl and then with water. The organic layer was separated, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash chromatography (eluent petroleum ether/diethyl ether (7:3)). Two fractions were recovered: the chromium pentacarbonyl pyridine complex (35%) and (+)-3-phenyl-5-oxotetrahydrofuran (**9o**). Data for **9o**: white crystals, mp 58-60 °C (79%); $[\alpha]_D = +50.9°$ (T = 60%; c = 1.03, chloroform) (lit.[18a] $[\alpha]_D = +52°$ (c = 0.4, chloroform)).

Synthesis of (−)-2-((*p*-Nitrobenzoxy)methyl)-5-oxotetrahydrofuran (9p). To a solution of (2*R*)-(−)-5-oxo-2-tetrahydrofuranoic acid (3.84 mmol) in 7 mL of anhydrous tetrahydrofuran was slowly added 2.2 mL (4.4 mmol) of a 2 M solution of borane-dimethyl sulfide at room temperature. After 4 h, 5 mL of methanol was added and the solvent distilled off at atmospheric pressure. The addition of methanol and the distillation were repeated until a colorless oil was obtained. The crude alcohol was dissolved in 10 mL of pyridine, and *p*-nitrobenzoyl chloride (3.84 mmol) was added to the solution; the mixture was heated to 75 °C for 30 min and then left at room temperature for 16 h. The solution was poured into 40 mL of 10% HCl and the white precipitate extracted with dichloromethane. The organic layer was washed with 120 mL of a saturated solution of $NaHCO_3$ and then with water to neutral pH, separated, dried over Na_2SO_4, and evaporated under reduced pressure. The residue crystallized from benzene/*n*-hexane, yielding compound **9p**: mp 145-147 °C (85%); $[\alpha]_D = -45.4°$ (T = 60%; c = 0.39, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.9-2.2 (m, 2 H, $CH_2C{=}O$), 2.3-2.8 (m, 2 H, $CH_2CH_2C{=}O$), 4.3-4.7 (m, 2 H, CH_2O), 5.0-5.8 (m, 1 H, CH), 8.1-8.4 (m, 4 H, arom); IR (Nujol) 1770 (CO of lactone), 1730 (CO of ester), 1530, 1350 (NO_2) cm^{-1}.

Acknowledgment. We wish to thank Dr. Paolo Cremonesi for part of the experimental work and the Italian Ministry of Education and the CNR of Rome for financial support.

Notes

Heterosilsesquioxanes: Synthesis and Characterization of Group 15 Containing Polyhedral Oligosilsesquioxanes

Frank J. Feher* and Theodore A. Budzichowski†

Department of Chemistry, University of California, Irvine, California 92717

Received June 12, 1990

Summary: The reactions of $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$ (**1**) with PCl_3, $AsCl_3$, and $SbCl_3$ give high yields of the corresponding pnictite esters, $[(c\text{-}C_6H_{11})_7Si_7O_{12}M]$, M = P (**2**), As (**3**), Sb (**4**). The bismuth congener, $[(c\text{-}C_6H_{11})_7Si_7O_{12}Bi]$ (**5**), was prepared by the reaction of **1** with $(t\text{-}BuO)_3Bi$. A single-crystal X-ray diffraction study of **2** reveals an interesting molecular structure with 1 of the 12 framework oxygen atoms lying inside the cube defined by the Si and P atoms. Phosphite **2** forms a 1:1 adduct with Me_3Al and is quantitatively oxidized to phosphate $[(c\text{-}C_6H_{11})_7Si_7O_{12}PO]$ (**7**) by ozone.

We recently reported practical syntheses of several incompletely condensed polyhedral oligosilsesquioxanes as part of our efforts to develop homogeneous models for silica surfaces.[1] The focal point of most of our research has been trisilanol 1, which exhibits many geometric similarities to potential sites of coordination available on idealized surfaces of known SiO_2 polymorphs (e.g., (111) cristobalite and (0001) tridymite).[1a] Since trisilanol 1 is formally derived from the hydrolytic removal of one silicon atom from a stable octameric "T_8" silsesquioxane, it exhibits a strong tendency to undergo reactions to fill the vacant vertex. Alkyltrichlorosilanes, alkyltrichlorogermanes, and alkyltrichlorostannanes,[1a] as well as a variety of main-group[1c,d] and transition-metal complexes,[1e] all undergo high-yield "corner-capping" reactions with 1. In this paper, we report the synthesis of polyhedral heterosilsesquioxanes, where the vacant vertex presented by 1 is occupied by group 15 representative elements.

Results and Discussion

The reactions of 1 with PCl_3, $AsCl_3$, and $SbCl_3$ in Et_3N/C_6H_6 afford virtually quantitative (NMR) yields of the expected pnictite esters (i.e., 2-4). All of these compounds give molecular ions in the electron impact mass spectrum and exhibit ^1H, ^{13}C, and ^{29}Si NMR spectra that are characteristic of cyclohexyl-substituted silsesquioxanes with apparent C_{3v} molecular symmetry. Bismite 5 can be prepared by the reaction of 1 with $(t\text{-BuO})_3Bi$.[2] It is

---

[†] Recipient of a Fannie and John Hertz Predoctoral Fellowship.

(1) (a) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741-8. (b) Feher, F. J.; Newman, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1931-6. (c) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 7288-9. (d) Feher, F. J.; Weller, K. J. *Organometallics* **1990**, *9*, 2638-40. (e) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3850-2.

(2) Evans, W. J.; Hain, J.; Ziller, J. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1628-9.

0276-7333/91/2310-0812$02.50/0