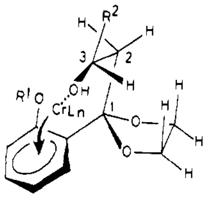
Table II. Diastereoselective Complexation of **6** with (Naphthalene)Cr(CO)$_3$

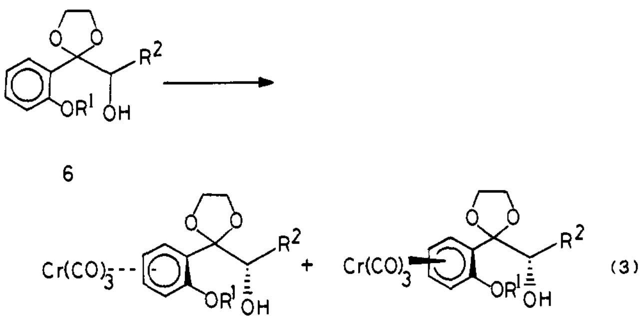
entry	R^1	R^2	ratio of **7**:**8**	yield (%)
1	Me	Me	85:15	80
2	Me	*n*-Bu	85:15	83
3	*i*-Pr	Me	92:8	88

operative for the high diastereoselective chromium complexation. The hydroxyl group of the side chain also plays an important function for high selectivity. Thus, the corresponding acetate of **2** (R^1 = Me, R^2 = Et, X = CH$_2$CH$_2$) gave a diastereomeric mixture in a ratio of 65:35. The appearance of high diastereoselectivity on the ligand exchange reaction can be explained by Cr(CO)$_3$ complexation via an intermediate **5**, in which the ethylene acetal (or *gem*-dimethyl) group is moved away from the *o*-alkoxyl group by rotation around the C(1)–C(Ar) bond due to steric effect, and the R^2 group is positioned to avoid severe steric interactions with the hydrogen atoms of ethylene acetal (or methyl) group.



5

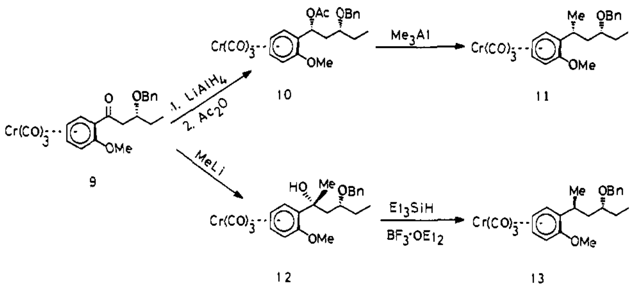
We next studied diastereoselective chromium complexation of the compounds **6**[11] with hydroxyl groups at the C-2 position of the alkyl side chain. In contrast to the above results (Table I), *S**,*S**-chromium complexes **7**[7] were predominantly obtained in these cases under the same reaction conditions (eq 3). The intermediate for complexation of **6** may be similar with **1** in which steric interactions between the *o*-alkoxy group and the alkyl group of the side chain are diminished by the spacial arrangement of these groups (Table II).



6

7 8

These chromium complexes prepared by the above ligand exchange reactions can undergo reactions in which control of the stereochemistry in the acyclic side chain is exhibited as follows. Protection of the hydroxyl group of the complex **3** (R^1 = Me, R^2 = Et, X = CH$_2$CH$_2$) by benzylation (BnBr/NaH/DMF/room temperature) and subsequent hydrolysis of the ethylene acetal (concentrated H$_2$SO$_4$/acetone/0 °C) gave an oily product **9** in 55% overall yield. Reduction of the carbonyl group of **9** with LiAlH$_4$ at −78 °C followed by acetylation afforded *S**,*R**,*R**-chromium complex **10** exclusively in 85% yield.[12] No trace of the corresponding epimeric complex at the benzylic position was detected. The treatment of **10** with Me$_3$Al in CH$_2$Cl$_2$ at −78 °C gave a single diastereomeric complex **11** as an oil in 50% yield. On the other hand, reaction of **9** with MeLi gave a single methylated complex **12** (mp 110 °C) which was converted to another diastereomeric *S**,*S**,*R**-complex **13** (mp 94 °C) in 75% yield by ionic hydrogenolysis (Et$_3$SiH/BF$_3$·OEt$_2$/CH$_2$Cl$_2$/−78 to 0 °C) without the formation of the epimeric syn isomer **11**. These syn and anti chromium complexes, **11** and **13**, are useful compounds for further acyclic stereocontrol, since the Cr(CO)$_3$-complexed anisole rings could be transformed into substituted cyclohexenone derivatives via stereo- and regioselective nucleophilic addition and subsequent protonation as developed by Semmelhack.[13]



Acknowledgment. We thank Dr. K. Hirotsu, Osaka City University, for X-ray crystallography of compounds **3** (R^1 = *i*-Pr, R^2 = Et, X = CH$_2$CH$_2$) and **7** (R^1 = *i*-Pr, R^2 = Me).

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[11] These compounds 6 were prepared by the following literature method: Cuvigny, T.; Larcheveque, M.; Normant, H. *Synthesis* **1978**, 857–858.

[12] The reduction of complex 9 with Zn(BH$_4$)$_2$ or NaBH$_4$ gave one diastereomeric chromium complex **10**.

[13] Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957–3965, and references cited therein.

Solid-State NMR Evidence for the Formation of Carbocations from Propene in Acidic Zeolite-Y

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Zeolites in the hydrogen form are widely used for such acid-catalyzed reactions as the cracking of alkanes, alkene isomerization, alkylation, and the conversion of methanol to hydrocarbons.[1] Although much of this chemistry can be explained via mechanisms involving carbocations, spectroscopic evidence for these intermediates in zeolites is limited. Earlier work by Leftin and Hall[2–4] on amorphous silica–alumina catalysts demonstrated, by using UV spectroscopy, that carbocations were formed upon adsorption of 1,1-diphenylethylene or triphenylmethane. More recently Maciel[5] has reported the ^{13}C CP-MAS spectrum of the triphenylmethyl carbocation following the surface reaction of triphenylchloromethane with silica–alumina.

From NMR studies remarkable progress has been made in understanding the chemistry of carbocations in solution. The ^{13}C spectra of carbenium ion centers are significantly deshielded; i.e., they are characterized by large positive chemical shifts. Both structural and dynamic information can be obtained from the magnitude of the chemical shifts. Similar information can be derived from NMR spectra of carbocations in the solid state, as demonstrated by the work of Myhre and Yannoni,[6] who formed *sec*-butyl and *tert*-butyl cations by codepositing 2-chlorobutane and antimony pentafluoride at low temperatures. The spectra indicate the presence of a dynamic *sec*-butyl cation at temperatures as low as −190 °C.

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[1] Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversion*; Academic Press: New York, 1981.

[2] Leftin, H. P.; Hall, W. K. *J. Phys. Chem.* **1962**, *66*, 1457.

[3] Leftin, H. P.; Hall, W. K. *Actes Congr. Int. Catal. 2nd* **1960**, *1*, 1353.

[4] Leftin, H. P.; Hall, W. K. *J. Catal.* **1967**, *8*, 394.

[5] Maciel, G. E. In *Heterogeneous Catalysis*; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, 1984; pp 349–381.

[6] Yannoni, C. S.; Myhre, P. C. *J. Am. Chem. Soc.* **1981**, *103*, 230.

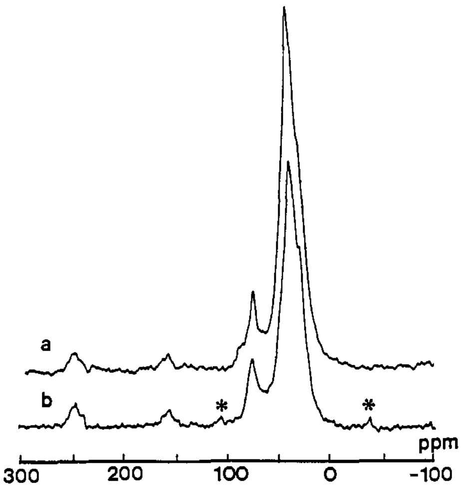


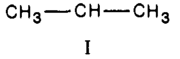
Figure 1. ^{13}C CP-MAS NMR spectrum of adsorbed propene-2-^{13}C: (a) H-Y zeolite and (b) ultrastable H-Y_u zeolite. * designates spinning sidebands.

In the present study we present CP-MAS NMR evidence both for dynamic and static carbocations which result from the reaction of propene in a H-Y zeolite. Previous infrared studies have shown that propene oligomerizes in acidic zeolites, even at 25 °C, to form molecules containing ca. 10 methylene units.[7] At higher temperatures (150–250 °C) aromatics were formed on H-ZSM-5 and H-mordenite, but on H-Y zeolites only coke was observed. The UV reflectance spectra of ethene or propene adsorbed on H-ZSM-5 and H-Y zeolites indicated the formation of cyclopentenyl and π-allyl carbocations, respectively.[8,9]

Both a normal H-Y zeolite and an ultrastable zeolite, H-Y_u, were employed in this investigation. The H-Y zeolite was prepared from an NH_4-Y zeolite (Si/Al = 2.5) by heating the sample under vacuum to 100 °C over a 2-h period. The temperature was then increased in 100 °C increments (1 h at each increment) to 400 °C. Partial dealumination of the zeolite by steaming at 600 °C for 1 h resulted in the H-Y_u zeolite (Si/Al = 4).[9] These samples were exchanged in 1 M NH_4NO_3 2 times at 70 °C to remove any residual sodium. After activation at 400 °C the acidic zeolites were cooled to 25 °C and exposed to 30–50 Torr of propene-2-^{13}C (99.2% enriched, MSD isotopes). Immediately after adsorption of propene the zeolites were transferred to a glovebox where they were packed under Ar into a Kel-F rotor. The spectra were acquired on a Chemagnetics M-100S solid-state NMR spectrometer, by using magic-angle spinning (2–3 kHz) with dry nitrogen gas.

The ^{13}C CP-MAS spectra[11,12] obtained following addition of propene to the H-Y and H-Y_u zeolites are shown in Figure 1 (parts a and b, respectively). Before discussing the interpretation of the spectra it is important to point out that extensive scrambling of ^{13}C occurs via a protonated cyclopropene intermediate.[6]

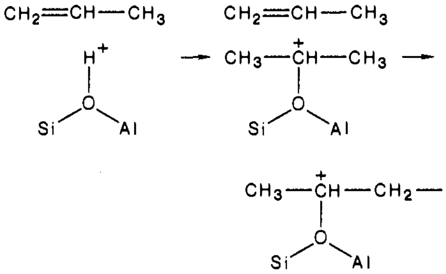
In Figure 1 we assign the peak at ca. 250 ppm to the isopropyl cation (I) which is formed on acidic sites immediately after adsorption. From the extensive solution-state studies of Olah and Donovan[13] it is apparent that static secondary alkyl cations should have a resonance at 300–330 ppm relative to TMS. In the zeolite, however, the carbocations strongly interact with the structural oxygen atoms of the zeolite in order to fulfill their role as charge-compensating cations. The interaction with the oxygen, although primarily ionic in nature, is believed to provide additional shielding for the observed ^{13}C nuclei which would shift the resonance upfield from that of the free carbocation. It has been shown that carbocations of the type RC^+OH exhibit a resonance approximately 80 ppm upfield from those having the structure RC^+R.[14] The methyl groups for I are typically at 48 ppm and in the spectra of Figure 1 would be part of the broad peak which is attributed to the oligomers (see below).



$$CH_3-\overset{+}{C}H-CH_3$$

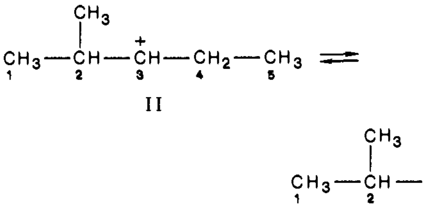
I

Once the isopropyl cation is formed, it can react with another physisorbed or gas-phase propene molecule, resulting in longer chain carbocations. This mechanism is shown in eq 1. The oligomerization continues until the zeolite cage is filled or until the opening into the cavities are blocked.



(1)

The peak at ca. 160 ppm is assigned to a dynamic carbocation (II $\rightleftarrows$ III) which is undergoing a degenerate exchange as demonstrated by using the equilibrium between the ethylisopropylcarbenium ion (II) and the methylisobutylcarbenium ion (III) as an example. Rapid exchange of the free alkyl cations would result in an average of the two static resonances at ca. 330 and 60 ppm.[13] The average value of 195 ppm is consistent with the observed resonance at 160 ppm if one again considers the effect of the framework oxygen. The peak at 70 ppm is assigned to the carbon which is β to the carbenium center.



$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{CH_3}{|}}{C}H}-\underset{3}{\overset{+}{C}H}-\underset{4}{CH_2}-\underset{5}{CH_3} \rightleftarrows \underset{1}{CH_3}-\underset{2}{\overset{\overset{CH_3}{|}}{C}H}-\underset{3}{CH_2}-\underset{4}{\overset{+}{C}H}-\underset{5}{CH_3}$$

II

III

(2)

The more intense peak at 40 ppm and the shoulder at 30 ppm result from methylene and methyl groups which are present in the higher molecular weight form of the neutral oligomers and the carbocations. The amplitude in this region of the spectrum was larger for the H-Y zeolite, which is consistent with the greater void volume of this material compared with the H-Y_u zeolite in which the cavities are partially blocked by *extra* framework aluminum.

Upon heating the sample to 220 °C for 20 min a strong peak appeared in the spectrum (not shown) at 140 ppm, which indicates the formation of aromatic compounds. This assignment is consistent with the infrared data of Ghosh and Kydd[7] which suggested that at this same temperature polycyclic aromatic compounds (i.e., coke) were formed from propene in a H-Y zeolite. It may not be possible, however, on the basis of chemical shift data to distinguish between simple aromatics and aromatic-derived coke.

In summary it appears that CP-MAS NMR provides a direct spectroscopic method for the identification of both static and dynamic carbocations in zeolites. The role of carbocations in the oligomerization of propene is supported by these results.

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(7) Ghosh, A. K.; Kydd, R. A. *J. Catal.* **1986**, *100*, 185.

(8) Vedrine, J. C.; Dejaifve, P.; Garbowski, E. D.; Drouane, E. G. In *Catalysis by Zeolites*; Imelik, B., et al., Ed.; 1980; pp 29–37.

(9) Garbowski, E. D.; Proliaud, H. J. *Chim. Phys.* **1979**, *76*, 687.

(10) Ward, J. W. U.S. Patent 3 929 672, 1975.

(11) For a review of the CP-MAS technique, see: (a) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201. (b) Maciel, G. E. *Science (Washington, DC)* **1984**, *226*, 282.

(12) The experimental conditions were as follows: 2-ms contact time, 1-s pulse delay, and 3000 scans per spectrum. Scans (3000) with change of spinning speed were also collected to identify the spinning sidebands.

(13) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5026.

(14) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; pp 225–227.

Acknowledgment. This research was supported by the U.S. Army Research Office and the Texas Advanced Technology Research Program. We are indebted to Paul Fritz for his help in preparing the zeolites and Gordon Campbell for his assistance with the NMR instrumentation.

Registry No. I, 19252-53-0; $H_2C=CHCH_3$, 115-07-1.

Total Synthesis of (−)-Specionin

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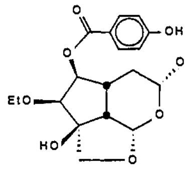
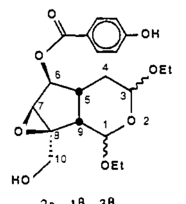
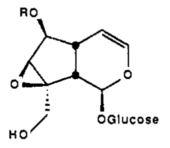
Specionin was isolated in 1983 by Nakanishi and Chang from the leaves of the *Catalpa speciosa* Warder tree.[2] This unusual iridoid has attracted interest because of its potent antifeedant activity against the Eastern spruce budworm, a common pest in North American forests. Isolated in only trace quantities, specionin was initially assigned structure **1** based on a detailed



1



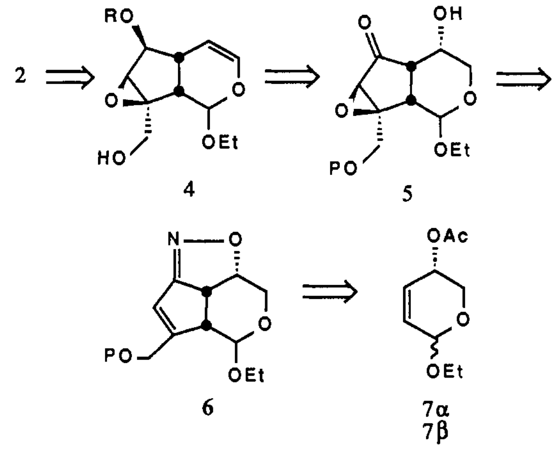
2a 1β, 3β
2b 1β, 3α
2c 1α, 3α
2d 1α, 3β



3a, R=H (catalpol)
b, R=COC$_6$H$_4$-p-(OH) (catalposide)

spectral analysis.[2] In 1985, a synthesis of compound **1** by Vandewalle and co-workers necessitated revision of the original proposal.[3a] Structure **2** was suggested, with the anomeric stereochemistry at C-1 and C-3 not absolutely certain. The common iridoid catalposide **3b** co-occurs with specionin, and it was indeed proposed that specionin might be an artifact of the ethanol extraction.[2] Structure **2** is consistent with this proposal. Very recently, Vandewalle has reported a racemic synthesis of the four possible anomers of specionin (**2a–d**) as well as the set of diastereomers epimeric at the epoxide-bearing carbons.[3b] With these diastereomers in hand, a detailed spectroscopic analysis permitted the assignment of specionin as the 1α,3β-isomer **2d**. We now report a stereoselective total synthesis of (−)-specionin which fully confirms the new structural assignment.

Scheme I



The key elements of a general approach to optically active iridoid aglucones are outlined in Scheme I.[4,5] One of our goals was the development of a method to introduce the enol acetal functionality embodied in the advanced intermediate **4**. Few methods exist for the introduction of this sensitive functional group,[6] which is present in many important iridoids such as catalpol (**3a**) and catalposide (**3b**). The precursor to **4** was envisioned to be β-hydroxy ketone **5**, which should be readily available by reduction of the corresponding Δ^2-isoxazoline **6**. In turn, **6** is prepared from **7**[7] by a variant of our recently developed Claisen/nitrile oxide sequence.[8]

While the anomeric stereochemistry of specionin was initially unclear, we felt that a trans disposition of the ethoxy groups was most likely (**2b** or **2d**).[9] Since our initial synthetic work directed at the structure **1** was performed by using 7β, we elected to prepare the 1β-isomers **2a** and **2b** with the advanced intermediates already in hand. Structures **2a** and **2b** were prepared by a sequence analogous to the one outlined in Scheme II.[10] Unfortunately, neither **2a** nor **2b** was identical with specionin; however, the synthesis did serve to confirm the structures of these two isomers in the Vandewalle mixture.[3b] This work convinced us that specionin must be **2d**. While acidic equilibration of **2a** and **2b** is conceivable, we elected to repeat the synthesis starting with 7α

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(1) (a) Alfred P. Sloan Foundation Fellow, 1985–87; Camille and Henry Dreyfus Teacher Scholar, 1986–91; Merck Faculty Development Awardee, 1986–87. (b) Mellon Fellow, 1986–87, University of Pittsburgh.

(2) (a) Chang, C. C.; Nakanishi, K. *J. Chem. Soc., Chem. Commun.* **1983**, 605. (b) Chang, C. C. Ph.D. Thesis, Columbia University, 1985. We thank Professor Nakanishi for a copy of this thesis.

(3) (a) Van der Eycken, E.; Callant, P.; Vandewalle, M. *Tetrahedron Lett.* **1985**, *26*, 367. (b) Van der Eycken, E.; Van der Eycken, J.; Vandewalle, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1719. Van der Eycken, E.; De Bruyn, A.; Van der Eycken, J.; Callant, P.; Vandewalle, M. *Tetrahedron* **1986**, *42*, 5385.

(4) (a) Most previous syntheses of iridoids can be classed into two strategies: oxidative cleavage of bicyclooctenes or [2 + 2] cycloaddition/retroaldol. For reviews, see: Paquette, L. A. *Top. Curr. Chem.* **1979**, *79*, 41. Thomas, A. F.; Bessiere, Y. In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1981; Vol. 4, pp 494–507. A new strategy based on Norrish I type cleavage of norbornanones has recently been developed by Vandewalle, see: ref 3. (b) For reviews on the structure and biological activity of iridoids, see: Bobbitt, J. M.; Segebarth, K. P. *Cyclopentanoid Terpene Derivatives*; Marcell Dekker: New York, 1969. El-Naggar, L. J.; Beil, J. L. *J. Nat. Products* **1980**, *42*, 649. Sticher, O. *New Natural Products and Plant Drugs with Pharmacological, Biological, and Therapeutic Activity*; Wagner, H., Wolff, P., Eds.; Springer-Verlag: New York, 1977; p 145.

(5) For recent developments in formation of the glycoside linkage, see: Tietze, L.-F.; Fischer, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 888. Battersby, A. R.; Westcott, N. D.; Glüsenkamp, K. H.; Tietze, L.-F. *Chem. Ber.* **1981**, *114*, 3439.

(6) Most past syntheses have been of iridoids possessing a carbomethoxy group at C-4. These compounds are more stable as evidenced by the ability to hydrolyze the glucoside without decomposition of the aglucone (see ref 4). For a recent preparation of the C-4 unsubstituted enol acetal by acetate pyrolysis, see: Trost, B. M.; Balkovec, J. M.; Mao, M. K.-T. *J. Am. Chem. Soc.* **1986**, *108*, 4974.

(7) The requisite starting materials, 7α and 7β, are readily available from D-xylal by Ferrier rearrangement. Fraser-Reid, B.; McLean, A.; Usherwood, E. W.; Yunker, M. *Can. J. Chem.* **1970**, *48*, 2877.

(8) Curran, D. P.; Jacobs, P. B. *Tetrahedron Lett.* **1985**, *26*, 2031.

(9) In a chair-like conformation, *cis*-**2a** should have both ethoxy groups equatorial-like and will profit from no anomeric effects. *cis*-**2c** should have both ethoxy groups axial-like and will suffer from unfavorable dipole interactions. See: Baker, R.; Brimble, M. A.; Robinson, J. A. *Tetrahedron Lett.* **1985**, *26*, 2115. For a detailed discussion of the stereochemistry and conformations of **2a–d**, see ref 3b.

(10) Jacobs, P. B., Ph.D. Thesis, University of Pittsburgh, 1986. Complete details of this work will be reported in a future full paper.

0002-7863/87/1509-5280$01.50/0