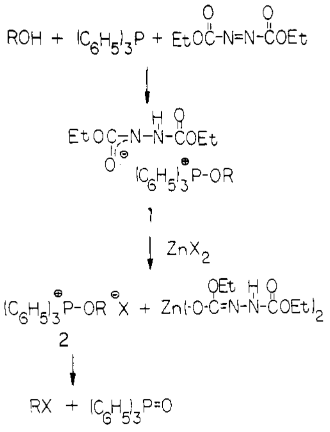
Scheme I



Primary, secondary, and allylic alcohols under the same conditions have been converted in good yields into the corresponding halides. The reaction is generally complete in minutes at room temperature. The generality of this effective procedure for the preparation of halides is apparent from the results compiled in Table I. We emphasize that the reaction conditions employed are sufficiently mild for acid- and base-sensitive molecules. Thus, sensitive unsaturated alcohols such as **3** and **4** (entries 1 and 2) are stable under these conditions and were converted in good yields into the allylic halides **9** and **10**, respectively. The preparation of β-phenylethyl chloride (**14**) from its alcohol (entry 5) with no detectable elimination illustrates further the mildness of the reaction conditions. The method works equally well with zinc bromide and iodide. Bromides or iodides were obtained in comparable yields, when zinc bromide or zinc iodide was used instead of zinc chloride under similar reaction conditions.

In summary, the present investigation has demonstrated that the use of diethyl azodicarboxylate, triphenylphosphine, and zinc halide constitutes a useful and convenient method for the halogenation of a wide variety of alcohols under very mild conditions.

Experimental Section

Preparation of 3α-Cholestanyl Chloride (13). (3α-Cholestanol (**6**, 390 mg, 1 mmol) and triphenylphosphine (790 mg, 43 mmol) were dissolved in anhydrous tetrahydrofuran (10 mL) under argon. Anhydrous zinc chloride (135 mg, 1 mmol) in 10 mL of tetrahydrofuran and diethyl azodicarboxylate (522 mg, 3 mmol) in 2 mL of tetrahydrofuran were added at room temperature consecutively. The mixture was stirred under argon at room temperature for 2 h. The reaction mixture was poured onto a short silica gel column and purified by chromatography with 1% ethyl acetate in hexane to give crystalline 3α-cholestanyl chloride (**13**) as the sole product (376 mg, 92%): mp 104 °C (lit. mp 105 °C); $[\alpha]_D$ +29° (c 4.89, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.65 (s, 3 H, CH_3), 0.78 (s, 3 H, CH_3), 0.86 (d, 6 H, J = 6 Hz, $CH(CH_3)_2$), 0.89 (d, 3 H, J = 6 Hz, CH_3), 0.75–2.00 (m, 31 H) 4.50 (m, 1 H, CHCl). Anal. Calcd for $C_{27}H_{47}Cl$: C, 79.66; H, 11.63. Found: C, 79.62; H, 11.64.

Generation of Halides from Alcohols. The conditions used for the generation of halides from alcohols were identical with those illustrated in the preparation of 3α-cholestanyl chloride (**13**). Yields and reaction times are compiled in Table I. Satisfactory spectral data were obtained for all new compounds. The synthesis of the dienyl alcohol **3** will be reported in a separated publication. Proton NMR data (δ) taken in $CDCl_3$ and analytical data include the following. **9**: 0.82 (t, 3 H, J = 6.5 Hz, CH_3) 1.05 (s, 9 H, t-Bu), 3.65 (t, 2 H, J = 5.9 Hz, $SiOCH_2$), 4.17 (d, 2 H, J = 8 Hz, CH_2Cl), 5.1–6.25 (m, 4 H, J = 15 Hz, J = 10 Hz, J = 8 Hz, vinyl protons), 7.35–7.65 (m, 10 Ar). Calcd for $C_{27}H_{37}ClOSi$ m/e 440, found m/e 440. **10**: 1.69 (s, 3 H, CH_3), 3.19 (s, 3 H, NCH_3), 3.32 (s, 2 H, benzylic), 3.65 (s, 3 H, $COOCH_3$), 3.90 (s, 3 H, OCH_3), 4.12 (d, 2 H, J = 7.8 Hz, CH_2Cl), 5.57 (br t, 1 H, J = 7.8 Hz, vinyl), 6.71 (s, 2 H, Ar). Calcd for $C_{15}H_{19}Cl_2NO_3$ m/e 331.0744, found m/e 331.0736. **11**: (s, 3 H, CH_3), 3.20 (s, 3 H, NCH_3), 3.30 (s, 2 H, benzylic), 3.65 (s, 3 H, $COOCH_3$), 3.89 (s, 3 H, OCH_3), 4.03 (d, 2 H, J = 8 Hz, CH_2Br), 5.61 (t, 1 H, J = 8 Hz, vinyl), 6.72 (s, 2 H, Ar). Calcd for $C_{15}H_{19}BrClNO_3$: C, 47.83; H, 5.08. Found: C, 47.75; H, 5.16. **14**: 3.01 (t, 2 H, J = 7.5 Hz, CH_2Ph), 3.68 (t, 2 H, J = 7.5 Hz, CH_2Cl), 7.18 (s, 5 H, Ar). **15**: 2.10–2.70 (m, 4 H, CH_2CH_2), 4.18 (m, 2 H, CH_2Cl), 4.82 (m, 1 H, CHOOC). Calcd for $C_5H_7ClO_2$: C, 45.31; H, 3.80. Found: C, 45.42; H, 3.72. **16**: 2.10–2.75 (m, 4 H, CH_2CH_2), 4.05 (m, 2 H, CH_2Br), 4.86 (m, 1 H, CHOOC). Calcd for $C_5H_7BrO_2$: C, 33.93; H, 2.85. Found: C, 33.98; H, 2.61. **17**: 2.20–2.75 (m, 4 H, CH_2CH_2), 3.95 (m, 2 H, CH_2I), 4.90 (m, 1 H, CHOOC). Calcd for $C_5H_7IO_2$: C, 26.81; H, 2.25. Found: C, 26.68; H, 2.48.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Registry No. **3**, 90605-46-2; **4**, 90605-47-3; **5**, 108-93-0; **6**, 80-97-7; **7**, 60-12-8; **8**, 10374-51-3; **9**, 90605-48-4; **10**, 90605-49-5; **11**, 90605-50-8; **12**, 542-18-7; **13**, 1474-58-4; **14**, 622-24-2; **15**, 39928-72-8; **16**, 32730-32-8; **17**, 1729-32-4; PPh_3, 603-35-0; $EtO_2CN{=}NCO_2Et$, 1972-28-7; $ZnCl_2$, 7646-85-7; $ZnBr_2$, 7699-45-8.

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Evidence of Side-Arm Involvement in Lariat Ether Complexes: A Lanthanide Shift Reagent Study

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Lariat ethers[1] are a class of macrocyclic polyether ligands whose structures consist of a side-arm group covalently bonded to a crown macroring. When the side arm contains one or more donor sites, binding cooperativity with the macroring is feasible, resulting in complexes of intermediate stability and microdynamic properties between those of simple crowns and those of the rigid bicyclic cryptands. This point has been addressed in previous work[2] using ^{13}C NMR T_1 measurements to monitor the individual mobilities of the carbon atoms in the free ligands as compared to those of corresponding alkali and alkaline-earth cation complexes. Previous results have clearly established the cooperative participation of the side arm in the complexation of the ring-bound cation in solution, reaching a maximum in cases where the location of the side-arm donor sites is optimized, the cation charge-to-size ratio is large, and the degree of rigidity of the "pivot" point (covalent attachment point of the side arm to the macroring) is minimized.[2] Participation of the side arm in the binding mechanism has also been unequivocally demonstrated in the solid phase by means of an X-ray study of lariat ether complexes.[3]

In order to expand our studies to trivalent cations and to obtain further confirmation of the side-arm participation

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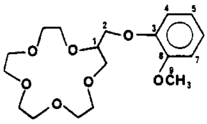
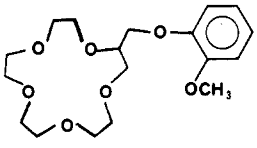
Table I. Lanthanide Induced NMR Shifts for Ligand 1 with $Yb(fod)_3$ in $CDCl_3$

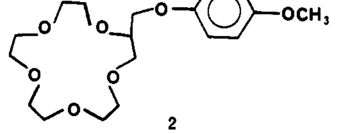


pos.	exptl data (δ), *r* 0	0.0830	0.190	0.302	calcd data δ_0	LIS	corr
3, 8	149.48	149.79	150.14	150.52	149.49	3.42 ± 0.04	0.9997
3, 8	148.35	148.67	149.11	149.60	148.34	4.13 ± 0.06	0.9996
5, 6	121.15	121.27	121.42	121.56	121.15	1.36 ± 0.02	0.9995
5, 6	120.61	120.78	120.88	120.98	120.64	1.18 ± 0.12	0.9787
4, 7	113.95	114.20	114.44	114.74	113.96	2.57 ± 0.06	0.9987
4, 7	112.05	112.20	112.35	112.49	112.06	1.44 ± 0.06	0.9968
1	78.46	79.34	81.48	83.78	78.17	18.01 ± 0.98	0.9932
9	55.71	55.83	55.98	56.08	55.72	1.24 ± 0.07	0.9941

in the binding process in solution, lanthanide NMR shift reagents were selected as probes for side-arm involvement in binding and as sources of the metal ions as well. Lanthanide shift reagents have been widely utilized in structural assignments, configurational assessment, and conformational analysis; thus, they seemed to be especially well suited for our purposes. Compounds 1 and 2 were selected for this study because of the ^{13}C NMR chemical shift differences between the aromatic side arm and the aliphatic macroring carbon atoms, a situation which greatly facilitates data analysis. In addition, these two ligands are structurally identical in all respects except for the position of attachment of the methoxy group on the aromatic ring. A substantial difference in the interaction of 1 and 2 with cations was anticipated because their homogeneous stability constants (K_s) with Na^+ in 90% MeOH are 927 and 364, respectively.



1



2

The selection of aromatic side arms introduces the possible complication of large contact contributions to the observed ^{13}C shifts. Since, contrary to dipolar interactions,[4] contact interactions do not follow a simple dependence on geometry,[5] it was necessary to use ytterbium shift reagents to minimize contact/dipolar shift ratios. In this report, $Yb(fod)_3$ was used to investigate the complexation processes of trivalent metal ions by lariat ethers 1 and 2 in a low polarity solvent, chloroform.

Experimental Section

Materials. Compounds 1 and 2 were synthesized by following procedures described elsewhere.[6] $Yb(fod)_3$ was obtained from Aldrich Chemical Company, dried in a vacuum oven at 110 °C for 24 h, and stored in a vacuum desiccator over phosphorus pentoxide. Deuteriochloroform (Aldrich) was stored over Linde 3A molecular sieves. All material transfers and sample preparations were performed in a drybox.

General Procedure. For maximium accuracy of the concentration measurements, four independent samples with ytterbium/ligand ratios ranging from 0.0 to 0.4 were prepared for each ligand. A typical sample was prepared by weighing a fixed amount of the ligand (0.21–0.23 mmol) in a glass vial, addition of the amount of ytterbium shift reagent needed to reach a given ratio, and dissolution of the mixture with 0.5 mL of $CDCl_3$. When complete dissolution was attained, the solution was syringed into a 5-mm o.d. NMR tube and the tube capped. After this, the sample was removed from the drybox and submitted to NMR analysis.

Nuclear Magnetic Resonance Spectroscopy. Natural abundance ^{13}C NMR spectra were recorded on a JEOL FX-90-Q spectrometer, operating at 22.50 MHz. The pulse width used was 7 μs, where a 9-μs pulse is equivalent to a 90° pulse. The spectral window was 4500 Hz and the acquisition time 0.91 s with 8K data points. Delays of 5 s were used after each pulse–acquisition sequence. The spectra were obtained under proton noise decoupling conditions and the chemical shifts were determined by using the center peak of the $CDCl_3$ triplet (77.03 ppm) as reference.

Calculations. For each ^{13}C resonance, chemical shift vs. ratio data points were fitted to the linear equation

$$\delta = Ar + \delta_0 \qquad (1)$$

where δ represents ^{13}C chemical shift, *r* is the ytterbium/ligand molar ratio, δ_0 stands for the chemical shift in the absence of shift reagent and, *A* is the slope. Linear least-squares analysis was utilized to fit the experimental data. Lanthanide induced shifts (corresponding to a 1:1 ratio) were determined as the slopes (*A*) from eq 1.

Results and Discussion

Experimental ^{13}C NMR chemical shifts for each ytterbium/ligand ratio and the values obtained from the linear regression analysis are given in Tables I and II. The assignment of resonances to specific carbon atoms was accomplished by using model compounds and assuming additive substituent effects on the aromatic carbons. In view of the similarity of electronic effects of both substituents on the aromatic ring, several resonances could not be unequivocally assigned, but this is not of concern in this work.

The effect of ytterbium addition on the crown macroring was monitored via the tertiary carbon (C-1). Since the side arm is attached at this point, its chemical shift is 8–10-ppm downfield from the remaining macroring carbon peaks which appear in an extremely narrow frequency range (71.2–68.9 ppm), precluding the possibility of individual

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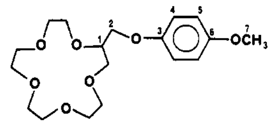
Table II. Lanthanide Induced NMR Shifts for Ligand 2 with Yb(fod)$_3$ in CDCl$_3$



	exptl data (δ), r =				calcd data		
pos.	0	0.123	0.196	0.340	δ$_0$	LIS	corr
6	153.70	153.84	153.84	153.94	153.72	0.67 ± 0.09	0.9650
3	152.88	153.21	153.21	153.65	152.90	2.24 ± 0.24	0.9970
4, 5	115.39	115.57	115.61	115.76	115.41	1.06 ± 0.08	0.9896
4, 5	114.36	114.49	114.49	114.54	114.39	0.50 ± 0.11	0.9189
1	77.96	80.41	82.12	85.39	77.86	21.98 ± 0.40	0.9994
7	55.48	55.55	55.50	55.50	55.50	0.02 ± 0.10	

assignments. Furthermore, broadening of these peaks is so severe, even at very low ytterbium/ligand ratios, that individual monitoring of any of these signals is virtually impossible. This is a good indication of a strong interaction between the ytterbium cation and the crown macroring, in excellent agreement with the behavior of these ligands in the presence of alkali and alkaline-earth metal ions. For ligand 1, this can be confirmed by the data in Table I; the largest lanthanide induced shift (LIS) is observed at C-1 (18.01 pm), while the remaining carbon atoms show much smaller LIS values. The same situation is also evident for ligand 2 (see Table II), and, overall, it can be stated that complexation of the ytterbium cation by both ligands proceeds mainly via strong interaction with the crown macroring. However, it must be pointed out that the LIS value (21.98 ppm) determined for the *p*-methoxy lariat is larger than that for the corresponding *o*-methoxy compound by 22%, even though binding constants suggest that 1 should form a stronger complex with sodium than 2 should. An explanation of this fact is presented below.

The LIS values determined for the side-arm carbon atoms (C-2 to C-9) are small and require a careful analysis. First of all, contact contributions, which are usually important when aromatic moieties are involved, are minimized by the selection of the shift reagent.[7] This point was further verified by performing several measurements with Eu(fod)$_3$ as LSR. Three- to fourfold enhancements of LIS values for the side-arm carbons were found while the macroring carbons did not show significant variations as compared to the results with Yb(fod)$_3$. The available evidence indicates that the present values are not significantly affected by contact interactions. Alternatively, the larger values for Eu could be the result of its larger size compared to Yb, giving rise to a more effective binding interaction with the lariat ether. It has also been reported that lanthanide induced shift ratios (LIR) afford more accurate structural information from the experimental data[8] since they are inherently less sensitive to the eventual presence of scavengers in the sample solutions than the absolute LIS values. Also, when contact contributions are negligible and dipolar shifts overwhelmingly predominate, the McConnell–Robertson equation[4] can be used to show that

$$\mathrm{DR} = (1/\mathrm{LIR})^{1/3} \qquad (2)$$

where DR is the ratio of distances of two specific carbon atoms from the ytterbium cation. This equation neglects the angular factor and, thus, its validity is limited to those cases where complete averaging of dipolar interactions throughout all possible spatial orientations is present.

Table III. Lanthanide Induced Ratios (LIR) and Distance Ratios (DR) for the Ytterbium Complexes of Ligands 1 and 2

ligand 1			ligand 2		
pos.	LIR	DR	pos.	LIR	DR
3, 8	0.190	1.74	6	0.030	3.22
3, 8	0.236	1.62	3	0.102	2.14
5, 6	0.076	2.36	4, 5	0.048	2.75
5, 6	0.066	2.47	4, 5	0.023	3.52
4, 7	0.143	1.91	1	1.000	1.00
4, 7	0.080	2.32	7	0.001	10
1	1.000	1.00			
9	0.069	2.44			

The lanthanide induced shift ratios and distance ratios for the ytterbium complexes of ligands 1 and 2 appear in Table III. All were calculated by taking as reference the LIS value of C-1 in each ligand. These values clearly demonstrate the different complexation patterns of both ligands. It is evident that the aromatic carbon atoms in 2 are not significantly perturbed by the ring-bound ytterbium cation and that the small effect observed is rapidly attenuated along the side-arm structure so that the terminal methoxy carbon exhibits a negligible LIS value. The latter result shows that the methoxy group is definitely not involved in the complexation process.

The LIS pattern for ligand 1 is strikingly different. This can be concluded from the LIR values of the aromatic ring carbons in which attenuation of the ytterbium effect is not so dramatic as that observed for ligand 2. Furthermore, the resonances corresponding to positions 3 and 8 show similar LIR values (~0.2), those for positions 4 and 7 are also similar and smaller (~0.1), and those for positions 5 and 6 are even smaller (~0.07). The methoxy carbon resonance is clearly affected by the presence of the ytterbium cation, in marked contrast with the results obtained for ligand 2. This is obviously a reflection of the methoxy substitution position in the benzene ring, which, when combined with the absolute LIS values of C-1 in both compounds, becomes clear evidence for side-arm involvement in ytterbium complexation by lariat ether 1. This is the only way to account for the smaller LIS value of the tertiary ring carbon in this ligand as compared to that of compound 2. When there is interaction of the side-arm oxygens with the ytterbium cation in the *o*-methoxy lariat, the macroring–cation binding characteristics are perturbed. These results indicate that, on the average, the ytterbium cation is closer to the "pivot" carbon atom in the complex with ligand 2 than it is in the complex with ligand 1. This is a consequence of the partial inhibition of the macroring–cation interaction by the competing side-arm–carbon interaction. Similar competing side-arm effects have been observed in other NMR studies of lariat ethers.[2].

As usual in LSR structural studies, certain assumptions were made. (1) A 1:1 stoichiometry was assumed for the

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ytterbium–ligand adducts. The consistency of the results obtained at low ytterbium/ligand ratios with those at higher ratios over the entire range investigated supports this assumption. (2) Although the nature of the interacting lanthanide reagent species cannot be unequivocally established nor critically inferred from these results, it seems likely that a large contribution from partially dissociated species, i.e., $Yb(fod)_2^+$ or $Yb(fod)^{2+}$ is present. The low polarity solvent does not favor dissociation of the shift reagent but the strong binding ability of the lariat ethers could surely enhance the stability of the dissociated species, perhaps even that of Yb^{3+}. This kind of ligand displacement reaction as opposed to the more common ligand number expansion, although unprecedented, would explain the relatively large LIS values of the side-arm carbon atoms. If the interacting species were $Yb(fod)_3$, it would be sterically difficult for the side-arm donor groups to interact with the lanthanide metal center. Further studies are currently underway to establish the nature of the interacting lanthanide reagent species with the lariat ethers.

Conclusions

The use of lanthanide shift reagents provides some insight into the structures of lanthanide ion complexes with lariat ethers. Ytterbium complexation by ligands 1 and 2 was studied by this novel approach. LIS data clearly indicate that the substitution position of the methoxy group in the benzene ring is the key to side-arm participation in the interaction with the ytterbium cation. In this way, our results demonstrate binding cooperativity in the case of the *o*-methoxy lariat (structure 1) while no such side-arm–ring cooperativity is evident for the *p*-methoxy lariat (structure 2). However, in both ligands, the crown macroring is, as expected, the main complexation site.

Acknowledgment. We gratefully acknowledge support of this work by NIH (to A.K., GM-08819; to L.E., RR-8102; to G.W.G., GM-31846). We also thank NSF (CHE-79-15201) for the funds used to purchase the NMR spectrometer.

Registry No. 1, 76719-75-0; 2, 76719-76-1; $Yb(fod)_3$, 18323-96-1.

Pyrolysis Studies of Organic Oxygenates. 5. Thermal Chemistry Pathways of 1-Naphthol under Hydrogen

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Received December 23, 1983

Previously we have investigated the thermal chemistry pathways of a number of ether systems under coal conversion like conditions.[1-4] In our studies on the pyrolysis of naphthalene methyl ethers[4] we identified three major pathways at 400 °C: O–C alkyl cleavage yielding naphthols and R–H upon hydrogen abstraction, an H–C alkyl abstraction/rearrangement pathway, and an isomerization pathway. The O–C alkyl cleavage is the most important thermal chemistry pathway.

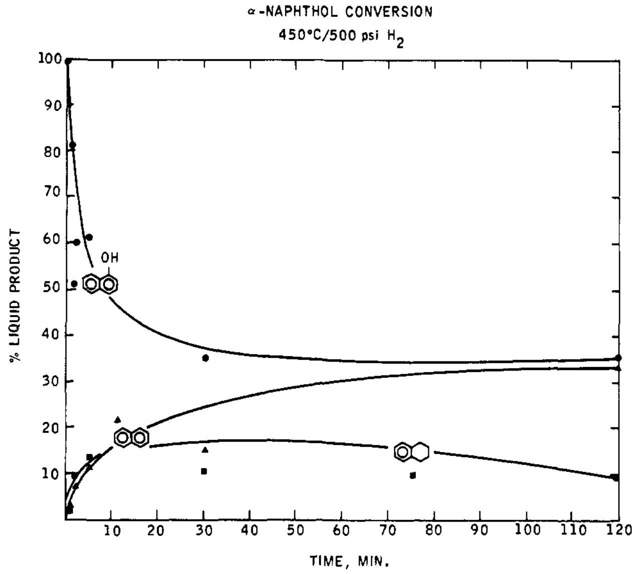

Figure 1.

In this paper we continue reporting our results on the thermal chemistry of reactive oxygenates representative of those species believed important in low-rank coals or coal conversion products. Here, we pursue the O–C alkyl cleavage pathway seen for ethers, to try to understand the important secondary reactions of the aryl alkyl ether system. In particular, we have studied 1-naphthol pyrolysis under coal conversion like conditions.

1-Naphthol was heated to 450 °C in a 30-cm^3 batch miniautoclave under an initial room temperature pressure of 3.5 MPa (500 psi) hydrogen. The pressure at reaction temperature was ~1000 psi. As shown in Figure 1, under our (largely) gas-phase conditions, the major products are naphthalene and tetralin. Other products identified include 1-tetralone and 1-tetralol. The presence of these two oxygenates is consistent with the results of Poutsma and Dyer[5] who studied 1-naphthol thermal chemistry without any external hydrogen at a temperature of 400 °C (where 1-naphthol exists largely in the liquid phase). Poutsma and Dyer showed only a 2% yield of naphthalene in a hydrogen starved system. This level of naphthalene is comparable to our yields of naphthalene from the thermolysis of naphthalene methyl ethers under an inert atmosphere.[4]

The tetralin yield diminishes with time (Figure 1) and that of naphthalene increases with time. This is consistent with hydrogen demand from unreacted naphthol and other hydrogen-starved systems (e.g., radicals, 1-tetralone, etc.) slowly dehydrogenating tetralin to naphthalene. At the moderate level of hydrogen pressure employed along with the high temperature of the experiments, hydrogen demand from the system appears to outstrip the ability of molecular hydrogen to replenish the hydroaromatic.

Under thermal conditions where Poutsma and Dyer[5] show about 33% conversion (75 min at 400 °C, no hydrogen), the major products are dinaphthylfuran (53%), 1-tetralone (18%), naphthalene (2%), and tetralin (3%). Under reaction conditions of 450 °C and 1000 psi of hydrogen at 39% conversion, we found tetralin (35%), naphthalene (28%), and 1-tetralone (10%) with 5% dimeric and higher molecular weight species. Clearly under

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