which was subjected to hydrolysis without further purification. 42: NMR 6.88 (dd, \( J = 4.4, 7.2, 1 \) H), 3.92 (m, H1, H5), 2.25 (dd, \( J = 4.4, 9.6, 14.1, 1 \) H), 2.07 (br s, 6 H, OAc), 1.75 (dd, \( J = 4.3, 7.2, 14.1, 1 \) H), 1.64 (br m, 4 H), 1.27 (br m, 2 H), 1.16 (d, \( J = 6.4, 6 \) H); IR 2926.1, 1766.7, 1433.5, 1375.8, 1250.7, 1204.7, 1127.0, 1058.3, 1013.7; MS (GCMS, CI); \( m/e \) (relative intensity) 245, (M + 1, 27), 185 (30), 144 (9), 143 (100).

\((2R, 6S)-\text{(trans-6-Methyltetrahydropyran-2-yl)acet-aldehyde} \) (43). Hydrolysis of 42 was carried out in a freshly prepared solution of sodium methoxide in methanol at room temperature for 5 min, followed by neutralization with methanolic solution of HCl. Solvent was removed under reduced pressure and the residue was extracted with ether to give 43 (60% overall yield from 41).

\[43: \text{NMR} \ 9.77 \ (dd, \ J = 1.8, 3.3, 3.0, \text{CHO}), 4.38 \ (m, \ J = 5.2, 8.7, 1 \ H), 3.93 \ (m, \ J = 3.3, 6.4, 1 \ H), 2.76 \ (dd, \ J = 15.9, 8.7, 3.3, 1 \ H), 2.45 \ (dd, \ J = 15.9, 5.2, 1.8, 1 \ H), 1.8-1.5 \ (m, 4 \ H), 1.3-1.1 \ (m, 2 \ H), 1.18 \ (d, \ J = 6.4, 6 \ H); \text{IR} \ 2922, 1687.1, 1581.9, 1430.0, 1366.3, 1281.2, 1216.6, 1166.6, 1068.1; \text{MS} : \text{m/e} \ (\text{relative intensity}) 142 (M^+, 3), 114 (5), 99 (23), 96 (12), 86 (10), 83 (10), 81 (53), 80 (5), 79 (9), 72 (6), 73 (11), 71 (20), 70 (20), 69 (17), 67 (9), 59 (6), 58 (12), 57 (18), 56 (9), 55 (100), 54 (56), 53 (10).

\((2R, 6S)-\text{(trans-6-Methyltetrahydropyran-2-yl)acetic Acid} \) (44). The aldehyde 43 was oxidized with Jones reagent in acetonitrile to give the corresponding acid 44 in 90% yield. This compound was found to be identical (\text{1H NMR, 13C NMR, IR, MS, optical rotation}) with an authentic sample synthesized earlier in these laboratories. 38, 42

Photochlorination of \( n \)-Alkanes Adsorbed on Pentasil Zeolites

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The photochlorination of \( n \)-alkanes adsorbed on pentasil zeolites proceeds with up to a 20-fold greater selectivity for the monochlorination of terminal methyl groups compared to the selectivity observed when the reaction is carried out in a homogeneous solution. This enhanced selectivity, which provides a novel means of synthesizing terminally functionalized linear alkanes, was found to be a function of the percent loading of the alkane on the zeolite, the zeolite’s silicon to aluminum ratio, the percent conversion of the starting material, and the water content of the zeolite.

Introduction

Recent advances in the chemistry of molecules adsorbed at interfaces are providing organic chemistry with a rich new array of concepts and opportunities that are serving to stimulate innovative approaches to synthetic methodologies and mechanistic investigations. 12 Molecular-sieve zeolites represent a novel and unique class of materials which are crystalline, yet porous, which possess enormous internal surface areas, and possess structures and compositions that can be varied over wide ranges. 3 In the case of the faujasite zeolites, the Si/Al ratio is routinely varied between 2 and 3 (the X family) and from 3 to 6 (the Y family). In the case of the pentasil (ZSM-5 family) zeolites, the subject of this report, the framework composition may be varied over a factor of 20,000 (from a Si/Al ratio of 5 to nearly infinity)! The ZSM-5 zeolites possess exceptionally high stability toward reaction with a variety of reagents and a nearly homogeneous internal surface (i.e., pure SiO\(_2\)) with hydrophobic selectivity. 5 Although representing only a small fraction of the tetrahedral atoms making up the framework, the framework aluminum atoms are crucial for the catalytic behavior of these materials. 4 It is reasonable to expect that a variety of unusual properties will accompany the variations in zeolite composition and in zeolite structure.

The ZSM-5 internal surface topology (Figure 1) consists of two types of pore systems (channels), both of which are composed of 10 tetrahedral-membered rings: one is sinusoidal with a nearly circular cross section of about 5.5 Å, and the other is straight and perpendicular to the sinusoidal channels. 5 The straight channels are roughly elliptical with dimensions of about 5.2 \( \times \) 5.8 Å. 6

The LZ-105 type zeolites are also considered to be members of the pentasil families and have been shown to adsorb straight-chain alkanes. 7 It seemed likely to us that the internal topology of the pentasil system would be conducive to reactions that were selective, since \( n \)-alkanes should be adsorbed within the channels in a manner that might protect the backbone CH\(_2\) groups from attack by reactive diffusing reagents such as chlorine atoms. In an overly simplistic view, the terminal methyl hydrogens, which are less reactive toward chlorine atoms than the secondary hydrogen in solution chlorination, might become more reactive because of the restrictions on diffusion of the chlorine atoms into the channels where they would

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encounter the methyl hydrogen atoms "head on". Computer-generated visualizations of dodecane adsorbed in one of the pentasil channels are shown in Figure 2.

Figure 1. Simplified representations of the LZ-105 channel system: left, three-dimensional representation of the internal void system; right, topological representation of the internal void system.

Figure 2. Side-view and axis-view representations of dodecane adsorbed in the straight channel of zeolite LZ-105, generated by using Chem-X molecular modelling software.11

In this paper we report that the photochlorination of long-chain n-alkanes adsorbed on the zeolite LZ-105 proceeds with a high degree of terminal (methyl) selectivity, which is not observed in the liquid-phase chlorination or in the thermal chlorination reaction of alkanes in other zeolite molecular sieves.5 We will discuss possible rationalizations for this selectivity as well as describing extensions of this methodology to the photochlorination of other, terminally substituted n-alkanes.

Results

The vapor-phase chromatogram shown in Figure 3 clearly demonstrates the product distributions that are obtained from the photochlorination of neat dodecane liquid (Figure 3A) and of dodecane adsorbed on a pentasil zeolite (Figure 3B). The most striking difference in the chromatograms is the higher selectivity for chlorination of primary (terminal) vs secondary (internal) carbon atoms when chlorination is conducted on the zeolite sample. In order to obtain information on the mechanistic aspects of the photochlorination of dodecane adsorbed on pentasil zeolites, we analyzed product distributions as a function of (1) the ratio of the weights of adsorbed dodecane to zeolite (termed loading); (2) the zeolite's silicon to aluminum ratio; (3) the percent contentation of the starting material; (4) the water content of the zeolite; and (5) the concentration of the chlorine in the reactor's atmosphere. In addition, the effect of substrate structure on the product distribution was investigated for n-alkanes of varying lengths and for terminally substituted dodecanes.

Figure 3. Gas chromatograms of the chlorination of dodecane: A, neat; B, adsorbed on zeolite LZ-105 (2% loading with Si/Al = 20); a, dodecane; b, 4-, 5-, and 6-chlorododecane; c, 2- and 3-chlorododecane; d, 1-chlorododecane; e, 1,2-dichlorododecane; f, 1,12-dichlorododecane.

| Table 1. Photochlorination of n-Dodecane on Zeolite LZ-105 |
|-------------------|-------------------|-------------------|-------------------|
| Loading (%)       | % Conversion (%)  | $S_m$ (%)         | $S_c$ (%)         |
| 0.5               | 40               | 33               | 5.7              |
| 1.0               | 51               | 52               | 5.0              |
| 1.1               | 50               | 60               | 7.8              |
| 2.0               | 35               | 48               | 5.9              |
| 3.0               | 36               | 56               | 3.5              |
| 4.5               | 34               | 62               | 2.3              |
| 6.0               | 32               | 56               | 1.8              |
| 10                | 32               | 63               | 1.4              |
| 20                | 36               | 78               | 1.2              |
| 30                | 33               | 70               | 1.5              |
| 40                | 26               | 73               | 1.7              |
| 50                | 32               | 84               | 1.8              |

*a* Weight percent of dodecane adsorbed on LZ-105. $S_m = \frac{\text{percent yield of monochlorinated products}}{\text{percent yield of monochlorinated dodecanes \times 3}}$.

Product Distributions for n-Alkanes. The ratios of chlorinated products varied as a function of various reaction conditions. It is convenient to define several selectivities in order to effectively discuss and compare the experimental data for reaction on zeolites and for reaction in solution. From the synthetic point of view, three types of selectivity parameters which are most pertinent to our investigations are (1) the total selectivity for terminal chlorination relative to internal chlorination in the monochlorination products ($S_i$); (2) the selectivity for monochlorinated products relative to the total chlorinated products ($S_m$); and (3) among the internally chlorinated

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products, the selectivity for the carbons at positions 2 and 3 over those at positions 4, 5, and 6 ($S_i$). In addition, we report data in terms of conventional percent chemical yields based on reacted starting materials.

As a benchmark, the value of $S_i$ for photochlorination of liquid dodecane is reported to be about 0.4. In contrast, the value of the terminal chlorination parameter, $S_{t}$, for dodecane adsorbed on LZ-105 zeolite (silicon to aluminum ratio of 24) was found to vary from 1.2 to 7.8 (Table I) as a function of coverage. The value of $S_i$ reached a maximum at loadings of about 1–2%, which corresponds to a 10–20% filling of the void space of the zeolite by the hydrocarbon. Above a few percent loading, the selectivity rapidly decreased to a limiting value of 1.2.

The decrease in terminal selectivity at higher loadings was shown by "isooctane washing" experiments to result from photochlorination of the dodecane adsorbed on or near the external surface of the zeolite. For example, washing a sample of LZ-105, which had been charged with dodecane, with isooctane (which is too bulky to enter the interior of the zeolite) followed by drying (at ambient temperature and pressure) and irradiation led to high selectivities even at initial high loadings. In these washing experiments, the terminal selectivity remained constant at $S_i = 5-6$ from (initial) 2–40% loadings. However, it was found that after washing of a sample containing an initial 20% loading of dodecane, approximately 2% was retained by the zeolite and the remainder was removed. These data demonstrate that LZ-105, which has not been dried by washing a sample of LZ-105, which had been charged with hydrocarbon at a 2% loading and by the zeolite and the remainder was removed. These data demonstrate that LZ-105, which has not been dried by washing, has been charged with hydrocarbon at a 2% loading and that the remaining adsorbed material is not associated with the internal surface.

In order to establish the relationship of the Si/Al ratio on the value of $S_i$ at a standard loading of 2%, we performed photochlorinations of dodecane on pentasil zeolites with silicon to aluminum ratios of Si/Al = 24 and 70 and Si/Al = 1220 (Silicalite). It was found that the best terminal selectivity (at 2% loading) was obtained for the lowest Si/Al (LZ-105); i.e., $S_i = 5.6$ for silicon to aluminum ratios of 24, 70, and 1220, respectively.

The terminal selectivity was also found to be dependent upon the percent conversion of the dodecane. At very low conversions, $S_i$ was very low (<2), and as the percent conversion increased, so did $S_i$ until it reached a maximum of about 7 at conversions of 40–60%. The value of $S_i$ then remained relatively constant up to conversions of 80%.

The effects of adsorbed water on $S_i$ were investigated by comparing "wet" and "dry" preparations. When the zeolite was baked in a muffle furnace at 500 °C for several hours, 5–10% of its weight was lost due to the evaporation of water. The sample was then rapidly treated with dodecane (2% loading), protected from atmospheric moisture, and photochlorinated. The same general trend for the value of $S_i$ that was found for the undried samples was also observed for the dried zeolites, except that the loading at which the maximal value of $S_i$ was observed was shifted from 1–2% to approximately 6%.

Experiments were performed in which the selectivity $S_i$ was monitored as a function of the chlorine charge (percent chlorine in the atmosphere employed for photochlorination). It was found that in the range from 0.5 to 100% halogen Si was completely insensitive to the Cl$_2$

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Table II. Effect of Chain Length on the Photochlorination of Alkanes, CH$_3$(CH$_2$)$_n$CH$_3$, Adsorbed on Zeolite LZ-105

<table>
<thead>
<tr>
<th>chain length (n)</th>
<th>% conversion</th>
<th>$S_i$</th>
<th>$S_{t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>21</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>13</td>
<td>30</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>18</td>
<td>18</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>20</td>
<td>44</td>
<td>25</td>
<td>8</td>
</tr>
</tbody>
</table>

*All experiments were run at a 2% loading on LZ-105 with a mixture of 0.7% chlorine in argon. All samples were exposed to 254-nm irradiation for 10 min. $S_m$ = percent yield of monochlorinated products. The other major product was 2-chlorododecanal, which was formed by a competing dark mechanism.

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Table III. Photochlorination of Substituted n-Alkanes in Zeolite LZ-105

<table>
<thead>
<tr>
<th>substrate</th>
<th>% conversion</th>
<th>$S_i$</th>
<th>$S_{t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-chlorododecane</td>
<td>41</td>
<td>86</td>
<td>2</td>
</tr>
<tr>
<td>1-bromododecane</td>
<td>19</td>
<td>26</td>
<td>7</td>
</tr>
<tr>
<td>dodecanenitrile</td>
<td>14</td>
<td>57</td>
<td>10</td>
</tr>
<tr>
<td>dodecanal</td>
<td>16</td>
<td>81</td>
<td>5</td>
</tr>
<tr>
<td>1-iodododecane</td>
<td>1</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

*All experiments were run at a 2% loading by weight of substrate on zeolite with a mixture containing 0.7% chlorine in argon. In all cases, the samples were exposed to 254-nm light for 10 min. $S_m$ = percent yield of monochlorinated products. Other products include multichlorinated and unidentified degradation products. $S_i$ = (percent yield of 12-chloroalkane × number of secondary hydrogens)/(percent yield of other monochlorinated alkanes × 6).

Importantly, this product is only a...
minor constituent of the dichlorinated products obtained in the photochlorination of neat dodecane (Figure 3). 1-Bromododecane showed a higher terminal selectivity (7), yielding 1-bromo-12-chlorododecane. Dodecanenitrile exhibited the highest observed terminal selectivity of 10, giving 12-chlorododecanenitrile, while the terminal methyl of dodecanal was chlorinated with $S_1 = 5$. In the case of dodecanal, the photoreaction proceeded in competition with a dark reaction, in which the methylene $\alpha$ to the aldehyde was chlorinated, giving 2-chlorododecanal.

**Discussion**

In contrast to the situation for homogeneous solutions, the notion of “concentration” is ill-defined for molecules adsorbed on high surface area porous solids. At the observational level, the “weight loading” or ratio of the weights of the adsorbed substrate to the porous solid is a quantity that corresponds most closely to the usual concentration terms for homogeneous solution. If the void volume of the porous solid is determined experimentally and if assumptions concerning the molecular dimensions (volume) of the substrate are made, the percent filling per void volume of the solid can be defined. The operational meaning of void space filling is difficult to establish a priori, since there is no guarantee, in the absence of confirming experimental evidence, as to whether the substrate will be homogeneously distributed. As a result of these ambiguities, we shall employ the weight loading as the operational term to describe the experimental systems at zero time. It is necessary to point out that as the reaction proceeds, a new ambiguity creeps in, namely, the site location of substrate molecules as a function of conversion and time. In spite of the fuzzy state of the structural and dynamic definition of the system, the synthetic potential of our results is manifest from Figure 3, and so we shall attempt to draw certain conclusions even though they are admittedly speculative.

First, we compare and discuss the results of photochlorination of dodecane adsorbed on pentasil zeolites with that for photochlorination of liquid dodecane. Since the ratio of products is a function of percent conversion and percent loading, we have selected 40–50% conversion for the liquid system and 2% loading for the zeolite system as standards for comparison. It is obvious from Figure 3 that chlorination of dodecane in the controlled environment of the zeolite greatly simplifies the monoclonorinated product distribution. In addition, the major product from the zeolite reaction (1-chlorododecane) was only a minor peak in the neat chlorination. This result is a major finding of this investigation, and the qualitative preference for terminal chlorination is preserved over a variety of experimental conditions.

Now let us consider the terminal selectivity, $S_1$, for dodecane at 2% loading as a function of the silicon to aluminum (Si/Al) ratio. The value of $S_1$ is high (7.8) for a low (Si/Al = 24) ratio and low (1.8) for the higher ratio (Si/Al = 70 or 1220). For comparison, the value of $S_1$ for photochlorination of neat dodecane is ca. 0.4 and is not a function of conversion for the monoclonorinated products. The occurrence of an “aluminum effect” suggests that the location of the dodecane is being influenced by the aluminum content of the zeolite. Typically, binding of substrates to the cation (Na+) associated with the negatively charged Al framework atoms is responsible for such effects.

We interpret these results as follows. On the basis of molecular modelling studies, the dodecane at ambient temperature and pressure is most likely resides in the straight channels of the pentasil zeolite (Figure 2). There is evidence, however, that at higher pressures the alkane will fill the sinusoidal channels. We propose that at low loadings (<2%) in the “dry” zeolite the dodecane is in a hydrophobic region (site I) of the zeolite. Thus, there is little influence of added water on the photochlorination. At intermediate loadings (<10%), the dodecane apparently occupies aluminum (cation) rich areas (site II) of the zeolite, and the photochlorination becomes sensitive to added water. At high (>10%) loadings, the internal surface is saturated with dodecane and the external surface (site III) serves as a new site for chlorination. At high loadings, the value of $S_1$ is determined by the sum of the selectivities at sites I, II, and III weighted by the populations at the three sites.

The above proposal is consistent with evidence in the literature that aluminum concentration gradients occur in very large ZSM-5 crystals, such that the lowest concentration occurs at the center of the crystal and the highest concentration occurs at the outside. All of the above evidence suggests that the zeolite crystals in this investigation possess a similar kind of structure. We also find that $S_1$ is inversely proportional to the bulk Al content of the zeolites. We suggest that the aluminum is important in the reaction either by controlling the position of the dodecane or by serving as a reaction site where the chlorine molecule is cleaved.

The answers to many questions regarding the details of the mechanism(s) of chlorination of molecules adsorbed on zeolites and related surfaces remain to be provided by future experiments. For example, with the data currently available, we cannot determine where the initial photolysis of the chlorine molecule occurs. Are the chlorine atoms generated in the gas phase outside of the zeolite, or are they generated inside of the zeolite? It is also possible that this step occurs at the interface between the zeolite surface and the gas phase. We are currently seeking to answer this and other questions regarding these interesting systems.

**Experimental Section**

**General.** The zeolites were obtained from the Union Carbide Corp. as LZ-105. Unless noted otherwise, the samples were used as received from the supplier without any further purification or drying.

**Photochlorination.** An appropriate aliquot of a long-chain hydrocarbon or substituted hydrocarbon in pentane was added to a weighed sample of zeolite. After standing at room temperature for at least 24 h, the pentane was removed under vacuum until the flask was no longer cool to the touch (excess pumping will remove the dodecane). For “dry” samples, the zeolite was dried to constant weight in a 500 °C oven. Upon addition of the pentane solution, the samples were evaporated to constant weight in a desiccator.

Two techniques were used for the actual chlorination step. For small samples, 10 mg of zeolite containing the reactant was purged with argon or nitrogen in a quartz reactor. After standing at room temperature for at least 24 h, the pentane was removed under vacuum until the flask was no longer cool to the touch (excess pumping will remove the dodecane). For “dry” samples, the zeolite was dried to constant weight in a 500 °C oven. Upon addition of the pentane solution, the samples were evaporated to constant weight in a desiccator.

The samples were agitated in a low-pressure Hg lamp for a measured amount of time. Upon completion of the reaction, the samples (usually 10 mg) were evacuated and purged with argon. They were then soaked in dichloromethane for at least 3 h, preferably overnight. The zeolite was removed by filtration and thoroughly rinsed with CH$_2$Cl$_2$. The solvent was evaporated (care

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was taken to avoid loss of product) and replaced with about 0.2 mL of hexane, and the sample was analyzed by gas chromatography.

For larger samples, a fluidized bed was employed. Quartz tubing fitted with a sintered-glass disk was connected to an oxygen-free nitrogen stream to which chlorine could be added. The zeolite sample (100-700 mg) was added to the bed and fluidized with nitrogen for 5 min. The sample was bathed in UV light from a low-pressure mercury lamp, and chlorine was slowly fed into the nitrogen stream at a controlled rate. After a measured amount of time, the light was turned off and the sample was purged with pure nitrogen. After being weighed, the samples were extracted with methylene chloride overnight and filtered as above. The samples were then diluted with 2-5 mL of hexane and analyzed by gas chromatography.

Analysis. Product ratios were determined with a Varian 3700 capillary gas chromatograph fitted with a 12-m SE-30 column and using a Hewlett-Packard 3390A integrator. For the chlorination of dodecane, product identification was made by coinjection of authentic samples. All assignments were confirmed by both NMR (Bruker AF 250) and GC-MS (Hewlett-Packard 5888A) in both EI and CI modes.

Acknowledgment. We thank the Union Carbide Corporation for their generous contribution of zeolite samples, Dr. Jordan Spencer for his helpful comments and advice, and the Air Force Office of Scientific Research, the National Science Foundation, and the Department of Energy for their generous support of this research. A.M.B. thanks the Swiss NSF for a travel grant under project 2.660.85.

Registry No. CH3(CH2)10CH3, 112-40-3; CH3(CH2)12CH3, 629-50-5; CH3(CH2)10CH2OH, 593-45-3; CH3(CH2)16CH3, 112-95-8; CH3(CH2)10Cl, 112-52-7; CH3(CH2)12Br, 143-15-7; CH3(CH2)10CN, 2437-25-4; CH3(CH2)12CHO, 112-54-9; Cl(CH2)12Cl, 3922-28-9; CH3(CH2)12Cl, 822-15-9; CH3(CH2)12Br, 3288-55-2; CH3(CH2)12Cl, 42217-02-7; 1-bromo-12-chlorododecane, 115141-70-3; 12-chlorododecanitrile, 115141-71-4; 2-chlorododecanal, 16486-86-5.

The He(I) Photoelectron Spectra of Methylene cyclopropene Derivatives. Correlation with Electrochemical Oxidation

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The He(I) photoelectron spectra of benzo and naphtho derivatives of 1,1-diphenylmethylene cyclopropene (DPMC) are presented. A correlation of electrochemical oxidation potentials (E1/2** values) and gas-phase ionization potentials of a series of aromatic hydrocarbons is discussed. This correlation suggests that the difference in E1/2** values for the two DPMC derivatives is due to structure-specific solvation of the radical cations. HAM/3 and HAM/3/CI calculations are compared with a simple structure-derived analysis of the observed photoelectron spectra. It is suggested that the effects of the fused cyclopropene groups are to be found in small (≈−0.2 eV) reductions of the second or higher ionization energies.

Methylene cyclopropene (1), the smallest nonalternant hydrocarbon, has recently been prepared, 1 and spectral observations 2 have confirmed the existence of a significant dipolar (1a) contribution to its ground-state electronic structure. Characterization of 1 → 1a is complicated by its moderately high chemical reactivity, but relatively complete spectral and theoretical determinations for this system are possible and forthcoming. 3 The present work concerns results on the kinetically stable cyclopropenanes 2 and 3, the diarylated benzo and naphtho derivatives of 1. 4

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3

The stability, imparted by the aryl substitution, allowed some of us to study 5 the electrochemical behavior of 2 and

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(3) An account of the observed photoelectron spectrum of 1 is currently submitted. S. Staley, private communication.