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Surface-Mediated Reactions. 6. Effects of Silica Gel and Alumina on Acid-Catalyzed Reactions[1]

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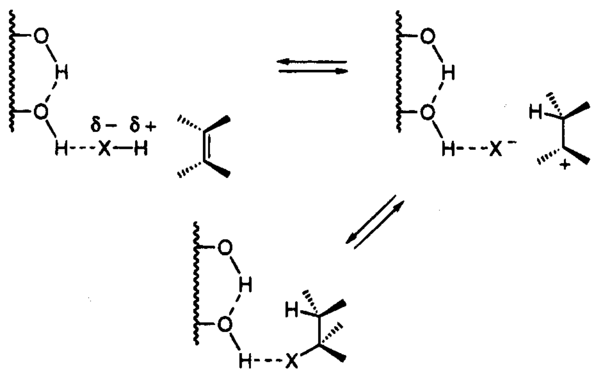
Adsorption of a variety of acids to chromatographic silica gel results in substantial enhancement of their catalytic activity—affording easily prepared, environmentally benign heterogeneous acids that are highly effective in mediating a number of processes. This was shown for the isomerization of allene **1** and dimerization of the corresponding 1,3-diene **2**; cyclization of (*R*)-citronellal (**5**), the related diester **10**, and 1,5-cyclooctadiene (**15**); Rupe rearrangement of alkynol **18**; and Friedel−Crafts cyclodehydration of alcohols **21**. By contrast, commercially available Nafion-H was significantly less effective as a heterogeneous acid catalyst. Chromatographic alumina displayed enigmatic behavior, showing enhanced acidity on the adsorption of HCl but little or no acidity on the adsorption of a variety of other types of acid. The results are discussed in terms of the surface structures of silica gel and alumina.

Recent studies in these laboratories have shown that chromatographic silica gel and alumina greatly facilitate the addition of hydrogen halides to alkenes and alkynes.[2] The hydrogen halides are adsorbed to silica gel and alumina surfaces through a hydrogen bonding interaction in which OH groups on the surface serve as hydrogen bond donors (Scheme 1). This interaction greatly enhances the acidity of the hydrogen halide by disrupting any aggregation that occurs in solution and polarizing the H−X bond, leading to protonation of the alkene or alkyne followed by transfer of halide ion to the resulting carbocation.[3] Adsorption of other acids, less likely to undergo addition, should similarly result in increased acidity, affording readily available heterogeneous acid catalysts.[4] We report here the use of silica gel to facilitate a variety of acid-catalyzed reactions, along with surprisingly different behavior by alumina.

Results

Rearrangement of Allene 1 and Dimerization of Diene 2. The surface of silica gel itself is mildly acidic.[5] Thus the highly acid-sensitive allene **1** isomerized to the 1,3-diene **2** in the presence of appropriately prepared silica gel (Table 1).[6] By contrast, the less reactive diene **2** was recovered unchanged from similar treatment with silica gel or with 1.0 mol equiv of CH_3CO_2H in CH_2Cl_2 solution. However, addition of silica gel to the latter solution resulted in the known acid-catalyzed dimerization to adduct **3**.[7] Transient amounts of the intermediate acyclic adducts **4**[7a] were also observed. Thus adsorption to silica gel enhanced the acidity of CH_3CO_2H, affording a mild but effective heterogeneous acid catalyst.

Scheme 1



Cyclization of (*R*)-Citronellal (5) and Diester 10. Ene-type cyclization of unsaturated carbonyl compounds, such as (*R*)-citronellal (**5**)[5a,8] and the related diester **10**,[9] has been used extensively in synthesis. Lewis acids have commonly been used to catalyze these reactions.[10] However, two reports of such cyclizations occurring during

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.

[1] Part 5: Breton, G. W.; Fields, J. D.; Kropp, P. J. *Tetrahedron Lett.* In Press.

[2] (a) Kropp, P. J.; Daus, K. A.; Tubergen, M. W.; Kepler, K. D.; Wilson, V. P.; Craig, S. L.; Baillargeon, M. M.; Breton, G. W. *J. Am. Chem. Soc.* **1993**, *114*, 3071−3079. (b) Kropp, P. J.; Crawford, S. D. *J. Org. Chem.* **1994**, *59*, 3102−3112.

[3] The surface also provides an exceptionally polar local environment. See: (a) Lindley, S. M.; Flowers, C. G.; Leffler, J. E. *J. Org. Chem.* **1985**, *50*, 607−610. (b) Spange, S.; Keutel, D.; Simon, F. *J. Chim. Phys. Phys.−Chim. Biol.* **1992** *89*, 1615−1622.

[4] For a review of heterogeneous acid catalysis, see Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. *New Solid Acts and Bases: Their Catalytic Properties*; Studies in Surface Science and Catalysis 51; Elsevier: Amsterdam, 1989.

[5] For some reported examples of acid-catalyzed reactions conducted using silica gel as the acid, see: (a) Chang, T.-C.; Washio, S.; Ueda, H. *Agr. Biol. Chem.* **1970**, *34*, 1734−1738. (b) Marshall, J. A.; Andersen, N. H.; Johnson, P. C. *J. Org. Chem.* **1970**, *35*, 186−191. (c) Andersen, N. H.; Ladner, D. W. *Synth. Commun.* **1978**, *8*, 449−461. (d) Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63−65. (e) Mangeney, P.; Alexakis, A.; Normant, J. F. *Tetrahedron* **1984**, *40*, 1803−1808. (f) D'Onofrio, F.; Scettri, A. *Synthesis* **1985**, 1159−1160. (g) Mook, R., Jr.; Sher, P. M. *Org. Synth.* **1987**, *66*, 75−86. (h) Schinzer, D.; Kalesse, M.; Kabbara, J. *Tetrahedron Lett.* **1988**, *29*, 5241−5244. (i) Pellet, M.; Huet, F. *Tetrahedron* **1988**, *44*, 4463−4468. (j) Mitra, R. B.; Reddy, G. B. *Synthesis* **1989**, 694−698. (k) Schinzer, D.; Kalesse, M. *Synlett* **1989**, 34−35. (l) Dauben, W. G.; Hendricks, R. T. *Tetrahedron Lett.* **1992**, *33*, 603−606.

[6] The acidity of silica gel is enhanced by drying at 120 °C to remove physisorbed water.[2a] However, drying at higher temperatures reduces acidity through the removal of chemisorbed water.

[7] (a) Hoffmann, H. M. R.; Vathke-Ernst, H. *Chem. Ber.* **1981**, *114*, 1182−1186. (b) Escher, A.; Übersax, B.; Neuenschwander, M. *Chimia* **1981**, *35*, 251−253. (c) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665−2667. (d) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993−7994. (e) Ghosh, S.; Bauld, N. L. *J. Catal.* **1985**, *95*, 300−304.

[8] (a) Schulte-Elte, K. H.; Ohloff, G. *Helv. Chim. Acta* **1967**, *50*, 153−165. (b) Nakatani, Y.; Kawashima, K. *Synthesis* **1978**, 147−148.

[9] (a) Tietze, L. F.; Beifuss, U. *Synthesis* **1988**, 359−362. (b) Tietze, L. F.; Beifuss, U.; Ruther, M. *J. Org. Chem.* **1989**, *54*, 3120−3129.

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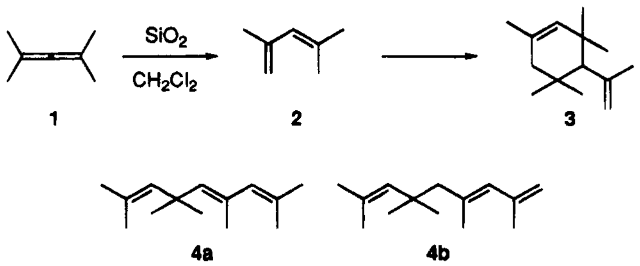
Table 1. Isomerization of Allene 1 and Dimerization of Diene 2[a]



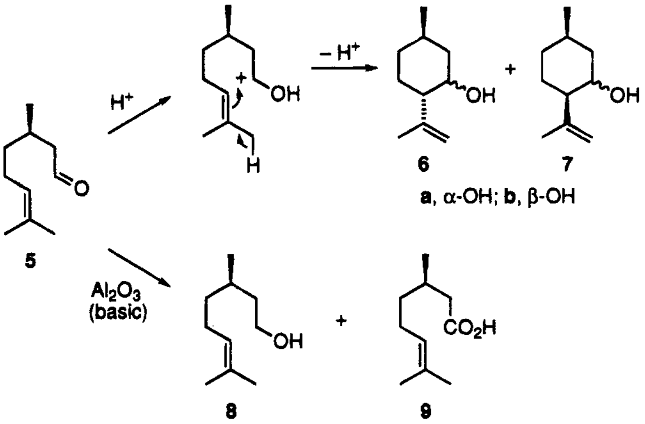
substrate	adsorbent	acid	time, h	yield, %[b] 1	2	3	4
1	SiO_2		4	84	16	*c*	
			24	52	41	7	*c*
2	SiO_2		24		97	*c*	
2		$CH_3CO_2H^d$	24		100		
2	SiO_2^e	$CH_3CO_2H^d$	4		52	44	4
			24		6	76	

[a] Conducted according to the standard small-scale procedure described previously.[2a] [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] Trace. [d] 1.0 mol equiv. [e] Added to the preceding solution after 24 h.

chromatography of unsaturated aldehydes over silica gel suggest that surface-mediated cyclization might be a convenient alternative to the use of heavy-metal catalysts.[5b,c] In an effort to expand to scope of using silica gel as a mild acid catalyst, Dauben and Hendricks have recently reported that treatment of (*R*)-citronellal (**5**) and diester **10** with silica gel under 15 kbar of pressure resulted in cyclization to a mixture of alcohols **6** and diesters **11** and **12**, respectively.[51] The use of high pressure was reportedly necessary to increase the acidity of the adsorbent. We found, however that cyclization of (*R*)-citronellal (**5**) to a similar mixture of alcohols **6**, along with a small amount of isomer **7a**, occurred readily at atmospheric pressure over appropriately prepared silica gel (Table 2). Cyclization occurred even faster over silica gel to which 0.1 mmol equiv of H_3PO_4 had been adsorbed. Although some reaction occurred in the presence of this concentration of H_3PO_4 in solution, cyclization was substantially faster in the presence of silica gel. Thus the presence of silica gel enhanced the effective acidity of H_3PO_4.

Over basic alumina (*R*)-citronellal (**5**) underwent instead slow reduction to (*R*)-*β*-citronellol (**8**).[11] However, over alumina that had been partially neutralized with HCl, or treated with sufficient $(COCl)_2$ to effect partial neutralization with the HCl generated in situ,[12] (*R*)-citronellal (**5**) readily afforded instead the cyclization products **6** and **7**.

Table 2. Cyclization of (*R*)-Citronellal (5)[a]



reagent	equiv[d]	adsorbent	solvent	time, h	yield, %[b] 5	6 + 7	distribution, %[c] 6a	6b	7a	7b
		SiO_2^e	CH_2Cl_2	48		73	20	80		
		SiO_2	CH_2Cl_2	4	2	83	17	79	4	
$H_3PO_4^f$	0.10		CH_2Cl_2	1	72	24	38	59	3	
$H_3PO_4^f$	0.10	SiO_2	CH_2Cl_2	1	3	82	36	61	3	
		Al_2O_3	CH_2Cl_2	16	19	*g*				
CH_3SO_3H	0.90	Al_2O_3	CH_2Cl_2	16	15	45[h]	32	61	3	4
HCl	0.90	Al_2O_3	$(C_2H_5)_2O$	0.5	12	77	22	68	5	5
$(COCl)_2$	0.45	Al_2O_3	$(C_2H_5)_2O$	0.1	5	76	22	66	6	6
$(COCl)_2$	0.45	Al_2O_3	CH_2Cl_2	0.5		95	23	66	7	4

[a] Conducted according to the procedure described in the Experimental Section, unless otherwise indicated. [b] Isolated by column chromatography. [c] Determined by HPLC analysis of the isolated mixture of products **6** and **7**. [d] [Reagent]/[**5**]. [e] Conducted at 15 kbar; see ref 51. [f] Anhydrous. [g] None detectable; (*R*)-*β*-citronellol (**8**) obtained in 39% yield. [h] (*R*)-*β*-citronellol (**8**) also obtained (3% yield).

The related diester **10** similarly afforded a mixture of the cyclized products **11** and **12** over silica gel at atmospheric pressure. Also formed was a minor product tentatively assigned the bicyclic structure **13** arising from secondary cyclization of the primary product **11** (Table 3).[13] As with (*R*)-citronellal (**5**), cyclization occurred more rapidly over silica gel in the presence of H_3PO_4. By contrast, little reaction occurred under similar conditions in the absence of silica gel. Treatment of diester **10** with Brønsted acids was previously found to afford only lactone **14**, from secondary reaction of the initial cyclization product **11**.[9a] This side reaction was almost completely avoided with H_3PO_4 over silica gel. However, use of the stronger acid CH_3SO_3H with silica gel resulted in substantial formation of lactone **14**, along with a mixture of cyclization products **11**–**13**. Once again, no detectable cyclization occurred over basic alumina, but rapid cyclization of diester **10** occurred over alumina that had been treated with sufficient $(COCl)_2$ to effect partial neutralization. However, the major cyclization product **11** was formed with lower selectivity than over silica gel.

Cyclization of (*Z,Z*)-1,5-Cyclooctadiene (15). Because of the proximity of the two double bonds in the preferred conformation of diene **15**, protonation of one double bond leads to transannular addition of the resulting carbocation **16** to the second double bond, ultimately affording the bicyclooctene **17**. However, this efficient route to the 5/5 fused ring system of **17** from the readily available diene **15** is thwarted by the sensitivity of the product toward acid-catalyzed polymerization. Being more strained and lacking the electron-withdrawing effect of the second double bond, bicyclooctene **17** is more readily protonated than the starting diene **15**. However,

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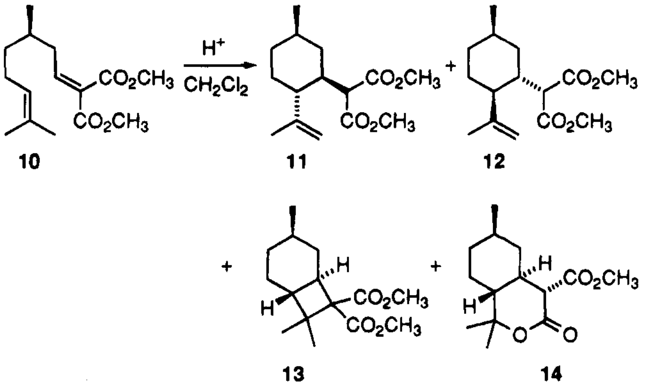
(10) See, for example: Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426–432.

(11) This was presumably accompanied by the oxidation product (*R*)-citronellic acid (**9**), which was bound to the surface. For previous examples of Cannizzaro oxidation/reduction of aldehydes over alumina, see: (a) Nayak, U. R.; Dev, S. *Tetrahedron* **1963**, *19*, 2293–2300. (b) Joshi, V. S.; Damodaran, N. P.; Dev, S. *Tetrahedron* **1968**, *24*, 5817–5830. (c) Kuiper, A. E. T.; Medema, J.; van Bokhoven, J. J. G. M. *J. Catal.* **1973**, *29*, 40–48. (d) Lamb, F. A.; Cote, P. N.; Slutsky, B.; Vittimberga, B. M. *J. Org. Chem.* **1974**, *18*, 2796–2797. (e) Joshi, V. S.; Dev, S. *Tetrahedron* **1977**, *33*, 2955–2957. (f) Ando, T.; Clark, J. M.; Cork, D. G.; Kimura, T. *Chem. Lett.* **1987**, 1315–1316.

(12) The 2.5 g of Fisher A540 alumina used under our standard conditions neutralizes 1.0 equiv of a hydrogen halide.[2]

(13) For a precedent, see ref 9b.

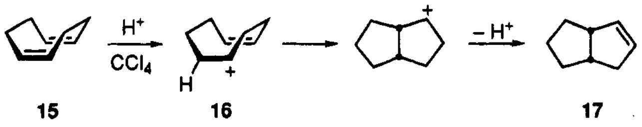
Table 3. Cyclization of Diester 10[a]



reagent	equiv[c]	adsorbent	time, h	yield, %[b] 10	11	12	13	14	11/12
		SiO_2[d]	1.5	25	66	7			9.4
		SiO_2	24	38	21	1	6	*e*	21
H_3PO_4[f]	0.10		24	95	4	*g*	*g*	*e*	
H_3PO_4[f]	0.10	SiO_2	24	*g*	72	3	*e*	*g*	24
CH_3SO_3H	0.10	SiO_2	1	*g*	33	1	1	43	33
		Al_2O_3	0.5	80	*e*	*e*	*e*	*e*	
$(COCl)_2$	0.45	Al_2O_3	0.5	*g*	62	5	*e*	*e*	12

[a] Conducted according to the procedure described in the Experimental Section, unless otherwise indicated. [b] Based on HPLC analysis of a mixture of products that was isolated by column chromatography. [c] [Reagent]/[**10**]. [d] Conducted at 15 kbar; see ref 51. [e] None detectable. [f] Anhydrous. [g] Trace.

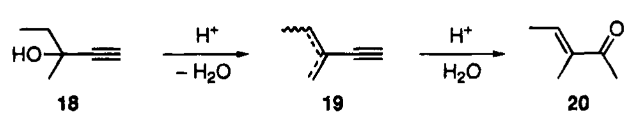
Table 4. Cyclization of (*Z,Z*)-1,5-Cyclooctadiene (15)[a]



acid	equiv[c]	adsorbent	time, h	yield, %[b] 15	17
H_3PO_4[d]	1.0		2	90	5[e]
H_3PO_4[d,f]	1.0	SiO_2	4	3	75[e]
H_3PO_4[d,f]	1.3	Al_2O_3	2	97	0
Nafion-H[g]	1.0		8	57	6[e]

[a] Conducted in refluxing CCl_4 according to the standard small-scale procedure described previously,[2a] except as indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Acid]/[**15**]. [d] 85% Aqueous solution. [e] Three unidentified minor products also obtained. [f] Acid added to adsorbent prior to the addition of diene **15**. [g] See ref 20.

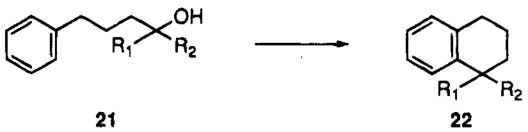
Table 5. Rupe Rearrangement of 3-Methyl-1-pentyn-3-ol (18)[a]



acid	equiv[c]	adsorbent	time, h	yield, %[b] 18	19	20
CH_3SO_3H	1.0		1.5	61	12	27
CH_3SO_3H	1.0	SiO_2	1.5		8	90
CH_3SO_3H	2.0	Al_2O_3	1.5	98		
Nafion-H[d]	1.0		16	90		
Nafion-H[d,e]			16	22	25	47

[a] Conducted as described in the Experimental Section for (*R*)-citronellal (**5**) and diester **10**, except that after the indicated reaction time 5 mL of 2-propanol was added and stirring continued for 20 min. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Acid]/[**18**]. [d] See ref 20. Regenerated according to the general procedure described in ref 18a. [e] Conducted in refluxing CCl_4 according to the procedure of ref 19.

Table 6. Cyclodehydration of Alcohols 21[a]



a, $R_1 = R_2 = H$; **b**, $R_1 = CH_3$, $R_2 = H$; **c**, $R_1 = R_2 = CH_3$

alcohol	acid	adsorbent	solvent	temp, °C	time, h	yield, %[b] 21	22
21a	CF_3SO_3H		CCl_4	77	4	94	6
21a	CF_3SO_3H	SiO_2	CCl_4	77	4	1	73
21a	CF_3SO_3H	SiO_2[c]	CCl_4	77	4	86	
21a	CF_3SO_3H[d]	Al_2O_3	CCl_4	77	4	96	
21b	CF_3SO_3H		CH_2Cl_2	25	4	92	8
21b	CF_3SO_3H	SiO_2	CH_2Cl_2	25	7	*e*	71
21c	H_3PO_4[f]		CH_2Cl_2	25	2	57	43
21c	H_3PO_4[f]	SiO_2	CH_2Cl_2	25	2		82
21c	H_3PO_4[f]	SiO_2[c]	CH_2Cl_2	25	2	91	8

[a] Conducted with 1.0 mol equiv of acid according to the procedure described in the Experimental Section. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] Treated with the indicated acid, filtered, washed with 2-propanol, and treated with alcohol **21** as outlined in the control procedure in the Experimental Section. [d] 2.0 mol equiv. [e] Trace. [f] Anhydrous.

treatment of diene **15** with silica gel in the presence of the weak acid H_3PO_4 readily afforded bicyclooctene **17** in high yield (Table 4). The more flexible diene **15** is apparently less sensitive than the rigid bicyclooctene **17** to steric effects inherent in undergoing surface-mediated protonation. Once again, little reaction occurred under the same conditions in the absence of SiO_2 or with H_3PO_4 in the presence of alumina.

Rupe Rearrangement of Alkynol 18. On treatment with acid, traditionally refluxing HCO_2H, alkynols such as **18** are converted to enones, via a process thought to involve dehydration followed by hydration of the resulting enyne.[14] The reaction is of synthetic interest since the required alkynols are readily prepared and enones are versatile intermediates, but the yields are highly variable. On treatment with CH_3SO_3H in solution alkynol **18** afforded a mixture of the enynes **19** and enone **20** (Table 5). Reaction occurred more rapidly in the presence of silica gel to afford enone **20** in excellent yield. Once again, no reaction occurred in the presence of alumina, even when pretreated with sufficient $SOCl_2$ to neutralize it with the HCl generated in situ.

Friedel–Crafts Cyclodehydration of Alcohols 21. Treatment of alcohols such as **21** with acid has long been a useful route to the corresponding tetralins.[15] As seen in Table 6, treatment of alcohols **21** with CF_3SO_3H or H_3PO_4 in the presence of silica gel readily afforded tetralins **22**. Substantially slower reaction occurred in the absence of silica gel, and alcohol **21a** underwent little reaction in the presence of alumina despite the presence of acid.

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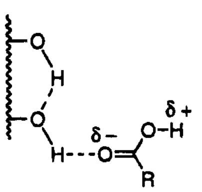
(14) For a review, see: Swaminathan, S.; Narayanan, K. V. *Chem. Rev.* **1971**, *71*, 429–438.

(15) (a) Bogert, M. T.; Davidson, D.; Apfelbaum, P. M. *J. Am. Chem. Soc.* **1934**, *56*, 959–963. (b) Roblin, R. O., Jr.; Davidson, D.; Bogert, M. T. *J. Am. Chem. Soc.* **1935**, *57*, 151–159.

Scheme 2

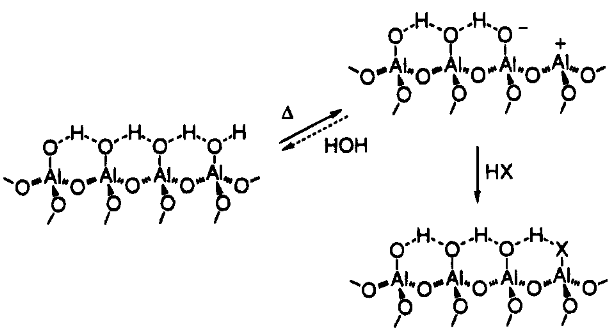


Discussion

Silica Gel. It is thus clear that adsorption of such acids as CH_3CO_2H, H_3PO_4, CH_3SO_3H, and CF_3SO_3H onto silica gel results in substantial enhancement of their acidities to afford easily prepared, highly effective heterogeneous acid catalysts. These catalysts are easily removed from reaction mixtures, and silica gel is both environmentally benign and readily recyclable. The increase in acidity is consistent with the acids being adsorbed to silica gel, like the hydrogen halides (Scheme 1),[2] through hydrogen bonding interactions in which surface silanol groups serve as hydrogen bond donors (Scheme 2).[16,17]

Comparison with Nafion-H. The superacidic perfluorinated sulfonic acid resin Nafion-H has been used extensively as a heterogeneous acid catalyst for organic transformations.[18] For example, treatment of alkynol **18** with Nafion-H in refluxing CCl_4 for 16 h was found to afford enone **20** in 83% yield.[19] However, the Nafion-H used was generated from a sample of the potassium salt that is not commercially available. Treatment of alkynol **18** under similar conditions with commercially available Nafion-H,[20] which had been regenerated as previously described,[18a] effected only slow conversion to enone **20** (Table 5). Similarly, the commercially available form effected cyclization of diene **15** to bicyclooctene **17** in only low yield (Table 4). By contrast, heterogeneous acid catalysts derived from adsorption of acids to silica gel are inexpensive, easily prepared, and highly effective.

Scheme 3



Alumina. Unlike silica gel, which is weakly acidic, chromatographic alumina is basic.[21] In addition to OH groups, the surface of alumina contains oxide ions in the outermost layer and exposed aluminum ions in the next lower layer, which are generated through the loss of chemisorbed water from neighboring OH groups on heating during the manufacturing process (Scheme 3).[22] One manifestation of the resulting basic character is the Cannizzaro oxidation/reduction exhibited by (*R*)-citronellal (**5**) and previously observed for a number of other aldehydes.[11] Another is that the first equivalent of an acid is consumed in neutralizing the basic surface.[2] Alumina neutralized with a hydrogen halide exhibits acidic character, apparently due to the formation of Al–X bonds adjacent to OH groups on the surface (Scheme 3).[23] Thus over alumina that had been treated with sufficient HCl or $(COCl)_2$ to effect partial neutralization, (*R*)-citronellal (**5**) and diester **10** readily afforded the cyclization products **6–7** and **11–12**, respectively.[24] Similarly, over alumina that had been partially neutralized with HCl, chloride **23** underwent rapid cyclization to tetralin **22c** (Table 7). Analogous behavior was exhibited over silica gel, which does not require prior neutralization to generate active sites. Cyclization in both cases presumably involves surface-mediated ionization of the chloride, corresponding to reversal of the last step of surface-mediated hydrohalogenation (Scheme 1), to generate carbocation **25**, which is subsequently trapped by the phenyl group.[25] By contrast, treatment of chloride **23** with alumina that had not been neutralized slowly afforded a mixture of alkenes **24** (Table 7).[26,27]

Surprisingly, alumina treated with other types of acids displayed little or no acidic behavior. Over alumina that had been neutralized with CH_3SO_3H, chloride **23** under-

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(16) For previous evidence for adsorption in this manner, see: Arnett, E. M.; Ahsan, T. *J. Am. Chem. Soc.* **1991**, *113*, 6861–6864. See also: Breton, G. W.; Daus, K. A.; Kropp, P. J. *J. Org. Chem.* **1992**, *57*, 6646–6649. As with the hydrogen halides,[2] adsorption presumably occurs preferentially to associated silanol groups, which are substantially more acidic than their isolated counterparts.

(17) Evidence has recently been presented that treatment of silica gel with a large excess of a variety of phosphorus acids, as well as with CH_3CO_2H and CF_3SO_3H, affords surface-bound esters: Lukes, I.; Borbaruah, M.; Quin, L. D. *J. Am. Chem. Soc.* **1994**, *116*, 1737–1741. However, this apparently does not occur to any significant extent under our conditions since esterification by sulfonic acids would result in neutralization of the acid. Moreover, treatment of silica gel with H_3PO_4 followed by washing with 2-propanol resulted in loss of its catalytic activity (Table 6).

(18) For reviews, see: (a) Olah, G. A.; Iyer, P. S.; Prakash, G. K. S. *Synthesis* **16**, 513–531. (b) Sondheimer, S. J.; Bunce, N. J.; Fyfe, C. A. *Rev. Macromol. Chem. Phys.* **1986**, *C26*, 353–413. (c) Waller, F. J. In *Polymeric Reagents and Catalysts*; Ford, W. T., Ed.; ACS Symposium Series 308; American Chemical Society: Washington, DC, 1986; Chapter 3.

(19) Olah, G. A.; Fung, A. P. *Synthesis* **1981**, 473–474.

(20) Nafion NR50, 10–35 mesh, hydrogen ion form, minimum ion exchange capacity of 0.8 mequiv/g.

(21) Chromatographic aluminas labeled neutral or acidic, based on the pH of a 10% aqueous slurry, have been partially neutralized with HCl during the manufacturing process.

(22) Scheme 3 is a partial representation of the surface structure of alumina. For reviews, see: (a) Knözinger, H. In *The Hydrogen Bond. III. Dynamics, Thermodynamics and Special Systems*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; Chapter 27. (d) Dufour, P.; Houtman, C.; Santini, C. C.; Nédez, C.; Basset, J. M.; Hsu, L. Y.; Shore, S. G. *J. Am. Chem. Soc.* **1992**, *114*, 4248–4257.

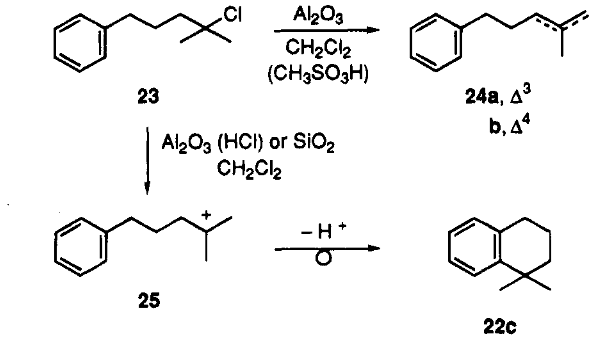
(23) F^- and Cl^- are known promoters of the surface acidity of alumina: Diddams, P. In *Solid Supports and Catalysts in Organic Synthesis*; Smith, K., Ed.; Ellis Horwood: New York, 1992; Chapter 1.

(24) Cyclization of (*R*)-citronellal (**5**) occurred more rapidly over alumina treated with $(COCl)_2$ than that treated with HCl, presumably due to the removal of some physisorbed water from the surface of the alumina during the hydrolysis of $(COCl)_2$. Physisorbed water competes with the substrate for adsorption to active sites.

(25) Any competing deprotonation of cation **25** to afford alkenes **24** would be followed by surface-mediated addition under these conditions to regenerate chloride **23**.

(26) For previous examples of dehydrohalogenation of alkyl halides over basic alumina, see ref 2a. See also: (a) Noller, H.; Hantsche, H.; Andréu, P. *J. Catal.* **1965**, *4*, 354–362. (b) Mochida, I.; Take, J.; Saito, Y.; Yoneda, Y. *J. Org. Chem.* **1967**, *32*, 3894–3898. (c) Mochida, I.; Anju, Y.; Yamamoto, H.; Kato, A.; Seiyama, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3305–3310. (d) Misono, M.; Yoneda, Y. *J. Catal.* **1974**, *33*, 474–479. (e) Mochida, I.; Anju, Y.; Kato, A.; Seiyama, T. *J. Org. Chem.* **1974**, *39*, 3785–3788. (f) Mochida, I.; Uchino, A.; Fujitsu, H.; Takeshita, K. *J. Catal.* **1976**, *43*, 264–272. (g) Paquette, L. A.; Park, H.; King, P. F. *J. Chem. Res., Miniprint* **1980**, 3580–3592. (h) Yanami, T.; Miyashita, M.; Yoshikoshi, A. J. *J. Org. Chem.* **1980**, *45*, 607–612. (i) Inokuchi, T.; Asanuma, G.; Torii, S. *J. Org. Chem.* **1982**, *47*, 4622–4626. (j) Ballinger, T. H.; Yates, J. T., Jr. *J. Phys. Chem.* **1992**, *96*, 1417–1423.

Table 7. Surface-Mediated Treatment of Chloride 23[a]



adsorbent	reagent[c]	equiv[d]	time, h	yield, %[b] 23	22c	24a	24b	24a/24b
SiO_2			4	49	48			
			24		97			
Al_2O_3			4	37	*e*	39	24	1.6
			24		5	69	25	2.8
Al_2O_3	CH_3SO_3H	1	8	64		21	15	1.4
			24	9	5	62	22	2.8
Al_2O_3	$SOCl_2$	0.45	4		99			
Al_2O_3	$(CH_3)_3SiNCS$	0.9	24		94			

[a] Conducted in $CDCl_3$ solution according to the standard small-scale procedure described previously.[2a] [b] Determined from integrations in the ^1H NMR spectrum, relative to those of an internal standard, of aliquots removed from the reaction mixture. [c] A slurry of Al_2O_3 in 1 mL of $CDCl_3$ containing the reagent was stirred for 20 min before the addition of chloride **23**. [d] [Reagent]/[**23**]. [e] Trace.

went slow dehydrohalogenation to the same mixture of alkenes **24** as obtained over untreated alumina, with no detectable formation of tetralin **22c**.[28] And diene **15**, alkynol **18**, and alcohol **21a** underwent no reaction on treatment over alumina in the presence of an excess of H_3PO_4, CH_3SO_3H, or CF_3SO_3H, respectively. Indeed, in the case of alkynol **18**, the presence of alumina inhibited the reactivity exhibited under homogeneous conditions by the acid alone. Even the highly acid-sensitive (*R*)-citronellal (**5**) underwent only very slow cyclization over alumina neutralized with CH_3SO_3H, compared with rapid cyclization over alumina partially neutralized with HCl.

This remarkable dichotomy in behavior between alumina neutralized with hydrogen halides on one hand and such acids as H_3PO_4, CH_3SO_3H, and CF_3SO_3H on the other is apparently related to an inability of the large conjugate bases of the latter acids to access, and bond with, the cationic sites of alumina. Thus chloride **23** underwent cyclization to tetralin **22c** over alumina treated with sufficient $(CH_3)_3SiNCS$ to effect partial neutralization by the HNCS generated on hydrolysis (Table 7). In this case, the conjugate base, being nearly linear, is apparently able to access the cationic sites.

The complex interactions between alumina and various types of acids is under further study as we continue to explore the rich chemical potential of silica gel and alumina surfaces.

Experimental Section

General Procedures. The procedures described previously were followed.[2a] HPLC analyses were performed with 4.8 mm x 25 cm columns packed with LiChrosorb Si 60 and a flow rate of 1 mL/min. Column chromatography was conducted on Merck grade 60 (230–400 mesh) silica gel. Surface-mediated procedures were conducted with Merck 10181 chromatographic silica gel (35–70 mesh, 675 m^2/g, 40 Å average pore diameter) or Fisher A540 chromatographic alumina (pH 9, 210 m^2/g) that had been equilibrated with the atmosphere at 120 °C for at least 48 h. Similar results were obtained with two or more different batches.

Rearrangement of 2,4-Dimethyl-2,3-pentadiene (1) and Dimerization of 2,4-Dimethyl-1,3-pentadiene (2). Treatment of allene **1** with silica gel as outlined in Table 1 followed by isolation by preparative gas chromatography (column A) afforded diene **2** as a colorless liquid that was identified by comparison with a commercial specimen.

Treatment of diene **2** with silica gel in the presence of CH_3CO_2H for 4 h as outlined in Table 1 followed by isolation by preparative gas chromatography (column A) afforded **1,3,3,5,5-pentamethyl-4-(1-methylethenyl)cyclohexene (3)** as a colorless liquid that was identified by comparison of its ^1H and ^{13}C NMR spectra with the data previously reported.[7a,29] The ^1H NMR spectrum of the crude reaction mixture exhibited peaks in the region of δ 4.8–5.7 that are assumed to be attributable to small amounts of **2,4,4,6,8-pentamethylnona-2,5,7-triene (4a)** and **-1,3,7-triene (4b)**.[7a]

Cyclization of (*R*)-3,7-Dimethyl-6-octenal [(*R*)-Citronellal] (5) and Methyl (5*R*)-2-(Methoxycarbonyl)-5,9-dimethyldeca-2,8-dienoate (10). A. Standard Procedure. To a 10-mL round-bottomed flask containing 2.5 g of silica gel or alumina that had been allowed to cool to 25 °C was added 4 mL of CH_2Cl_2, along with any indicated reagent, and the resulting mixture was stirred for 5 min. A solution of 1.0 mmol of aldehyde **5** or diester **10** in 1 mL of CH_2Cl_2 was added, and the resulting mixture was further stirred for the indicated amount of time. The reaction was quenched by the addition of 5 mL of ethyl acetate, the silica gel removed by vacuum filtration, and the separated adsorbent washed well with 20 mL of ethyl acetate and 40 mL of CH_2Cl_2. The combined organic fractions were washed with 30 mL of 5% Na_2CO_3 solution, filtered, and concentrated, followed by chromatography on silica gel (elution with 5:1 hexanes–ethyl acetate) to afford a mixture of cyclized products that was analyzed by HPLC (elution with 20:1 hexanes–ethyl acetate).

B. (*R*)-Citronellal (5). Treatment of (*R*)-citronellal (**5**) as outlined in Table 2 afforded a mixture of products **6** and **7** as a colorless oil. The presence of the minor isomers **7** was confirmed by ^1H NMR analysis of the mixture.

[1*S*-(1α,2β,5β)]-5-Methyl-2-(1-methylethenyl)cyclohexanol (7a): ^1H NMR (C*H*OH) δ 3.67 (dt, J = 10.4, 4.2 Hz); lit.[8a] δ 3.63 (m).

[1*R*-(1α,2α,5α)]-5-Methyl-2-(1-methylethenyl)cyclohexanol (7b): ^1H NMR (C*H*OH) δ 3.89 (br m); lit.[8a] δ 3.86 (m).

Chromatography on silica gel afforded, on careful elution with 5:1 hexanes–ethyl acetate, alcohols **6** as colorless liquids.

[1*S*-(1α,2α,5β)]-5-Methyl-2-(1-methylethenyl)cyclohexanol (6a): IR 3500 (br), 3100, 2930, 2870, 2845, 1710, 1640, 1450, 1375, 1120, 1025, 890, 730 cm^{-1}; ^1H NMR δ 4.95 and 4.78 (2 × br s, 2 H), 3.98 (br m, 1 H), 1.98 (m, 2 H), 1.78 (s, 3 H), 1.70 (m, 2 H), 1.50 (br s, 1 H), 1.45 (m, 1 H), 1.15 (m, 1 H), 0.92 (m, 2 H), 0.88 (d, J = 6.4 Hz, 3 H); lit.[8a] ^1H NMR 4.87 (m), 4.72 (m), 3.88 (br m), 1.77 (d, J = 1.0 Hz), 0.87 (d, J = 5.5 Hz).

[1*R*-(1α,2β,5α)]-5-Methyl-2-(1-methylethenyl)cyclohexanol (6b): IR 3400 (br), 3070, 2950, 2925, 1645, 1450, 1090, 1048, 1025, 885 cm^{-1}; ^1H NMR δ 4.86 (m, 1 H), 4.82 (br s, 1 H), 3.42 (dt, J = 4.3 and 10.4 Hz, 1 H), 2.01 (m, 1 H), 1.86 (m, 1 H), 1.69 (d, J = 1.1 Hz, 3 H), 1.65 (m, 2 H), 1.48 (m, 2 H), 1.30 (m, 1 H), 0.95 (m, 2 H), 0.92 (d, J = 6.5 Hz, 3 H); lit.[8b] IR 3560, 3450, 3070, 1640, 1050, 1020, 900 cm^{-1}; ^1H NMR δ 4.86

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(27) Suggestive of the involvement of a bulky base, there was substantial formation of the less highly substituted alkene **24b** during the early stages of reaction. However, since the alumina is being partially neutralized by the HCl byproduct during the course of elimination, competing acid-catalyzed elimination develops. This is reflected by an increase of the ratio **24a/24b** with time and the formation of small amounts of tetralin **22c** toward the end.

(28) The dehydrohalogenation of chloride **23** over alumina neutralized with CH_3SO_3H is clearly inconsistent with the proposed involvement of O^- sites in dehydrohalogenations over basic alumina.[26j] The mechanism of this reaction is under further study in these laboratories.

(29) Giguere, R. J.; von Ilsemann, G.; Hoffmann, H. M. R. *J. Org. Chem.* **1982**, *47*, 4948–4954.

(m, 2 H), 3.47 (dt, J = 4.5 and 10 Hz, 1 H), 1.72 (d, J = 0.5 Hz, 3 H), 0.95 (d, J = 5.5 Hz, 3 H).

(*R*)-3,7-Dimethyl-6-octen-1-ol (8) was obtained by chromatography as a colorless liquid that was identified by comparison with a commercial specimen.

C. Diester 10. Treatment of diester **10**[9] as outlined in Table 3 afforded a colorless liquid that was shown by its spectral properties to be a mixture of **dimethyl (1′*R*,2′*R*,5′*R*)-(11)** and **dimethyl (1′*S*,2′*S*,5′*R*)-2-(2′-isopropenyl-5′-methylcyclohex-1′-yl)propane-1,3-dioate (12)** in the manner described previously.[9]

1α,4α,6β-4,8,8-Trimethylbicyclo[4.2.0]octane-7,7-dicarboxylic acid, dimethyl ester (13) was isolated from the mixture as a colorless oil by HPLC: IR 2960, 1730, 1260 cm^{-1}; ^{1}H NMR δ 3.67 (s, 3 H), 3.66 (s, 3 H), 2.19 (dt, J = 12.1, 3.1 Hz, 1 H), 1.93 (dt, J = 12.1, 3.3 Hz, 1 H), 1.7 (m, 2 H), 1.5 (m, 2 H), 1.22 (s, 3 H), 1.02 (s, 3 H), 1.1 (m, 3 H), 0.87 (d, J = 6.6 Hz, 3 H). ^{13}C NMR δ 170.8, 169.7, 64.1, 51.7, 47.8, 46.8, 43.7, 35.6, 34.9, 33.3, 26.3, 23.9, 22.6, 20.1. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 67.33; H, 9.10.

4α,4aα,6β,8aβ-Octahydro-1,1,6-trimethyl-3-oxo-1*H*-2-benzopyran-4-carboxylic acid (14) was isolated by column chromatography as a colorless oil that was indistinguishable from a specimen prepared as described previously:[9] ^{1}H NMR δ 3.72 (s, 3 H), 3.00 (d, J = 11.3 Hz, 1 H), 2.09 (dq, J = 11.3, 3.7 Hz, 1 H), 1.73 (br t, J = 11 Hz, 3 H), 1.35 (s, 3 H), 1.29 (s, 3 H), 1.3 (m, 2 H), 1.0 (m, 2 H), 0.84 (d, J = 6.5 Hz, 3 H), 0.62 (q, J = 12.0 Hz, 1 H); ^{13}C NMR δ 169.5, 166.9, 86.4, 55.0, 52.5, 45.9, 40.5, 35.9, 34.1, 28.1, 27.1, 23.2, 21.9; lit.[9] no spectral data.

Preparative-Scale Cyclization of (*Z,Z*)-1,5-Cyclooctadiene (15). Into a 200-mL round-bottomed flask was weighed 25 g of silica gel. The flask was stoppered, and the contents allowed to cool to 25 °C. Fifty milliliters of CCl_4 was added, followed by 2.16 g (20 mmol) of diene **15**. The resulting suspension was stirred and 4.61 g (40 mmol) of 85% H_3PO_4 was added. The suspension was heated under reflux for 1 h, allowed to cool, and then filtered. The filtrate was washed with 3 × 25 mL of CH_2Cl_2, and the combined organic fractions were washed with 2 × 50 mL of saturated Na_2CO_3 solution and 50 mL of water. The combined aqueous washings were back extracted with 50 mL of CH_2Cl_2, and the combined organic fractions were dried over saturated NaCl solution followed by anhydrous Na_2SO_4 and concentrated by rotary evaporation. Isolation by preparative gas chromatography (column C) afforded ***cis*-1,2,3,3a,4,6a-hexahydropentalene (17)** as a colorless oil: IR 3050, 2940, 2860, 1620, 1469, 1450, 1353, 1333, 1296, 1272, 700 cm^{-1}; ^{1}H NMR δ 1.3, 1.4, and 1.7 (3 × m, 6 H), 2.0 (br d, J = 16 Hz, 1 H), 2.6 (m, 2 H), 3.1 (m, 1 H), 5.5 and 5.6 (2 × m, 2 H); ^{13}C NMR δ 25.2, 32.3, 35.7, 40.1, 41.0, 50.6, 129.4, 134.5; lit.[30] ^{13}C NMR ($CDCl_3$) δ 25.4, 32.5, 35.9, 40.4, 41.2, 50.8, 129.5, 134.7.

Preparative-Scale Rearrangement of 3-Methyl-1-pentyn-3-ol (18). Alkynol **18** was treated with silica gel in the presence of 0.96 g (10.0 mmol) of CH_3SO_3H for 1.5 h according to the standard preparative-scale previously described.[2a] The CH_2Cl_2 was removed by rotary evaporation, and the silica gel residue was placed on top of a 6 × 1-in. silica gel column and eluted with a 7:1 mixture of C_5H_{12} and $(C_2H_5)_2O$. Concentration by rotary evaporation afforded 0.78 g (70% yield) of **3-methyl-3-penten-2-one (20)** as a pale yellow liquid: IR 2929, 1662, 1424, 1388, 1372, 1356, 1265, 1125, 1074 cm^{-1}; ^{1}H NMR δ 1.73 (s, 3 H), 1.83 (d, J = 6.9 Hz, 3 H), 2.26 (s, 3 H), 6.72 (q, J = 6.9 Hz, 1 H); ^{13}C NMR δ 10.73, 14.78, 25.34, 138.36, 138.70, 199.71; lit.[31] ^{1}H NMR (CCl_4) δ 1.7 (m, 6 H), 2.18 (s, 3 H), 6.65 (q, J = 4.0 Hz).

Independent Preparation of Enynes 19. A solution containing 6.6 g (43 mmol) of $POCl_3$ in 10 mL of pyridine was added dropwise to an ice-cooled solution containing 1.5 g (15 mmol) of alkynol **18** in 5 mL of pyridine at such a rate as to maintain the temperature <20 °C. The resulting mixture was stirred at 25 °C for 2 h and then slowly poured over a mixture of ice and water (CAUTION: vigorous gas evolution). The aqueous layer was extracted with 2 × 50 mL of 2-methylbutane. The combined organic fractions were washed with 3 × 50 mL of water and dried over 2 × 25 mL of saturated NaCl followed by anhydrous Na_2SO_4. Removal of the solvent afforded a pale yellow liquid shown by gas chromatographic analysis (column A) to consist of a 1.0:5.5:1.5 mixture of (*E*)- and (*Z*)-3-methyl-3-penten-1-yne and 3-methylene-1-pentyne, respectively. Preparative gas chromatography afforded enynes **19** as colorless liquids.

(*E*)-3-Methyl-3-penten-1-yne: ^{1}H NMR δ 1.7 (br d, 3 H), 1.76 (br s, 3 H), 2.72 (s, 1 H), 6.0 (m, 1 H); lit.[32] no spectral data. **(*Z*)-3-Methyl-3-penten-1-yne:** ^{1}H NMR δ 1.82 (m, 6 H) 3.09 (s, 1 H), 5.78 (m, 1 H); lit.[32] no spectral data.

3-Methylene-1-pentyne: ^{1}H NMR δ 1.08 (t, 3 H), 2.18 (br q, 2 H), 2.88 (s, 1 H), 5.27 (br s, 1 H), 5.37 (br s, 1 H); lit.[33] ^{1}H NMR δ 2.15 (m), 2.8 (s,), 5.25 (m).

Reaction mixtures from the rearrangements of alkynol **18** described in Table 5 gave peaks having retention times identical with those of enzymes **19** on gas chromatographic analysis (column A).

Preparation of α-Methylbenzenebutanol (21b). To a mixture of 70 mg (1.8 mmol) of $LiAlH_4$ in 3 mL of anhydrous $(C_2H_5)_2O$ under an atmosphere of N_2 was added via cannula with rapid stirring a solution of 1.03 g (6.36 mmol) of 5-phenyl-2-pentanone, obtained as described below, in 2 mL of $(C_2H_5)_2O$. The resulting thick mixture was stirred for an additional 5 min, water was added dropwise to quench the excess $LiAlH_4$, and 3 mL of 10% H_2SO_4 was added. The organic layer was separated, and the aqueous layer was washed with 3 × 15 mL of $(C_2H_5)_2O$. The combined organic fractions were washed with 10 mL of saturated NaCl solution, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford a colorless liquid. Column chromatography afforded, on elution with 3:1 hexanes−ethyl acetate, 0.77 g (74% yield) of alcohol **21b** as a colorless liquid: IR (neat) 3350, 3020, 2965, 2915, 1600, 1490, 1450, 1370, 1125, 1085, 745, 695 cm^{-1}; ^{1}H NMR δ 7.25 (m, 2 H), 7.15 (m, 3 H), 3.75 (sextet, J = 6.1 Hz, 1 H), 2.61 (t, J = 7.5 Hz, 2 H), 1.80 (br s, OH, 1 H), 1.65 (m, 2 H), 1.45 (m, 2 H), 1.15 (d, J = 6.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 142.3, 128.3, 128.2, 125.6, 67.8, 38.8, 35.8, 27.4, 23.4; lit.[15b] no spectral data.

Preparation of α,α-Dimethylbenzenebutanol (21c). To a solution of 2.1 g (12 mmol) of benzenebutanoic acid in 100 mL of anhydrous THF at 0 °C under an atmosphere of N_2 was added dropwise 35 mL (49 mmol) of 1.4 M CH_3Li with stirring. The resulting colorless solution was stirred for an additional 2 h at 0 °C, warmed to 25 °C, and carefully poured into 500 mL of saturated NH_4Cl solution with rapid stirring. The organic layer was separated, and the aqueous layer was washed with 3 × 100 mL of $(C_2H_5)_2O$. The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated to afford a pale yellow oil. Column chromatography afforded on elution with 3:1 hexanes-ethyl acetate 1.03 g (52% yield) of **5-phenyl-2-pentanone:** IR 3030, 2940, 1718, 1605, 1495, 1453, 1368, 1158, 740, 695 cm^{-1}; ^{1}H NMR δ 7.37 (m, 2 H), 7.19 (m, 3 H), 2.62 (t, J = 7.4 Hz, 2 H), 2.43 (t, J = 7.4 Hz, 2 H), 2.11 (s, 3 H), 1.90 (quintet, J = 7.4 Hz, 2 H); ^{13}C NMR δ 207.9, 141.3, 128.1, 128.0, 125.6, 42.3, 34.7, 29.4, 24.9; lit.[34] IR 1710, 1605 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.10 (s, 5 H), 2.50 (m, 4 H), 2.00 (s, 3 H), 1.82 (t, J = 7 Hz, 2 H).

Continued elution afforded 0.91 g (42% yield) of alcohol **21c** as a colorless oil: IR 3400, 3040, 2980, 2940, 1605, 1500, 1455, 1380, 1200, 1150, 910, 745, 695 cm^{-1}; ^{1}H NMR δ 7.29 (m, 2 H), 7.20 (m, 3 H), 2.62 (t, J = 7.5 Hz, 2 H), 1.7 (m, 2 H), 1.5 (m, 2 H), 1.4 (br s, 1 H), 1.20 (s, 6 H); ^{13}C NMR δ 142.3, 128.2, 128.1, 125.6, 70.6, 43.3, 36.2, 29.1, 26.1; lit.[15a] no spectral data.

Cyclodehydration of Alcohols 21. A. Standard Procedure. The standard procedure for cyclization of (*R*)-citronellal (**5**) and diester **10** was followed except that reactions

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(30) Whitesell, J. K.; Matthews, R. S. *J. Org. Chem.* **1977**, *42*, 3878−3882.

(31) Hasbrouck, R. W.; Kiessling, A. D. A. *J. Org. Chem.* **1973**, *38*, 2103−2106.

(32) Bertrand, M.; Monti, H. *Tetrahedron Lett.* **1968**, 1069−1073.

(33) Mornet, R.; Gouin, L. *J. Organomet. Chem.* **1975**, *86*, 57−67.

(34) Hegedus, L. S.; Williams, R. E.; McGuire, M. A.; Hayashi, T. *J. Am. Chem. Soc.* **1980**, *102*, 4973−4979.

were quenched by the addition of 5 mL of 2-propanol followed by 10 min of stirring. The silica gel was allowed to settle, and 1 mL of the supernatant liquid was removed, neutralized over anhydrous Na_2CO_3 containing 2 drops of $(C_2H_5)_3N$, and analyzed by gas chromatography (column A).

B. Control Procedure. A slurry of 2.5 g of silica gel in 4 mL of solvent containing 1.0 mmol of CF_3SO_3H or H_3PO_4 was either heated under reflux for 4 h or stirred at 25 °C for 2 h, respectively, and then filtered. The silica gel was washed with 3 × 30 mL each of 2-propanol and CH_2Cl_2, dried under vacuum, and then added to 5 mL of solvent containing 1.0 mmol of alcohol **21a** or **21c**, respectively. The resulting mixtures were treated as outlined in Table 6, followed by workup and analysis as described in part A.

C. Characterization of Products. The reaction mixture was filtered and the silica gel was washed with 100 mL of CH_2Cl_2. The combined organic fractions were washed with 50 mL of 5% Na_2CO_3 solution, dried over anhydrous Na_2SO_4, and concentrated. Chromatography over silica gel afforded the products as colorless liquids on elution with hexanes.

Treatment of alcohol **21a** as outlined in Table 6 afforded **1,2,3,4-tetrahydronaphthalene (22a),** which was characterized by comparison with a commercial specimen.

Treatment of alcohol **21b** afforded **1-methyl-1,2,3,4-tetrahydronaphthalene (22b):** IR 3070, 3020, 2940, 2865, 1490, 1460, 1445, 1375, 1040, 750, 723 cm^{-1}; ^{1}H NMR δ 7.20 (m, 1 H), 7.09 (m, 3 H), 2.9 (m, 1 H), 2.75 (m, 2 H), 1.90 (m, 2 H), 1.76 (m, 1 H), 1.52 (m, 1 H), 1.28 (d, J = 7.0 Hz, 3 H); ^{13}C NMR δ 142.1, 136.7, 128.9, 128.0, 125.6, 125.3, 32.4, 31.5, 29.9, 22.8, 20.4; lit.[35] ^{13}C NMR δ 142.1, 136.1, 129.3, 128.3, 126.0, 125.8, 32.7, 31.8, 30.2, 23.0, 20.8.

Treatment of alcohol **21c** afforded **1,1-dimethyl-1,2,3,4-tetrahydronaphthalene (22c):** IR 3063, 3020, 2950, 2930, 1490, 1465, 1440, 1360, 1053, 755, 725 cm^{-1}; ^{1}H NMR δ 7.32 (br d, J = 7.4 Hz, 1 H), 7.13 (m, 1 H), 7.06 (m, 2 H), 2.76 (t, J = 6.4 Hz, 2 H), 1.81 (m, 2 H), 1.69 (m, 2 H), 1.28 (s, 6 H); ^{13}C NMR δ 145.7, 136.0, 129.0, 126.6, 125.8, 125.2, 39.4, 33.8, 31.8, 30.8, 19.8; lit.[35] ^{13}C NMR δ 145.7, 135.9, 129.3, 126.7, 126.1, 125.5, 39.6, 33.7, 31.9, 30.8, 19.9.

(4-Chloro-4-methyl-5-pentyl)benzene (23). A. Preparation. To a rapidly stirred mixture of 0.65 g (3.1 mmol) of PCl_5 and 0.32 g (3.2 mmol) of Na_2CO_3 in 3 mL of CH_2Cl_2 at 0 °C was added a solution of 0.47 g (2.6 mmol) of alcohol **21c** in 1 mL of CH_2Cl_2. After further stirring for 20 min, the mixture was filtered through a plug of glass wool and concentrated. Column chromatography afforded on elution with 5:1 hexanes–ethyl acetate 0.52 g (84% yield) of chloride **23** as a colorless liquid: IR (KBr) 2950, 1451, 1370, 1109, 690 cm^{-1}; ^{1}H NMR δ 7.3 (m, 2 H), 7.2 (m, 3 H), 2.62 (br t, J = 6.9 Hz, 2 H), 1.78 (m, 4 H), 1.54 (s, 6 H); ^{13}C NMR δ 142.0, 128.4, 128.3, 125.8, 70.8, 45.5, 35.8, 32.4, 26.8; lit.[36] no spectral data.

B. Surface-Mediated Treatment. From the reaction outlined in Table 7 tetralin **22c** and alkenes **24a,b** were isolated by preparative gas chromatography and identified by comparison with specimens prepared independently as described herein.

Independent Preparation of (4-Methyl-3-pentenyl)benzene (24a) and (4-Methyl-4-pentenyl)benzene (24b). To a solution of 1.49 g (8.36 mmol) of alcohol **21c** in 45 mL of pyridine was added 1.92 g (10 mmol) of 4-$CH_3C_6H_4SO_2Cl$. The resulting solution was heated to reflux for 24 h. Most of the pyridine was removed through distillation, and the residue was poured into 300 mL of $(C_2H_5)_2O$, washed with 8 × 150 mL of H_2O and 2 × 150 mL of saturated NaCl solution, dried over anhydrous Na_2SO_4, filtered, and concentrated. The resulting semisolid was triturated with hexane to separate the residual pyridinium tosylate salt and filtered. Column chromatography afforded on elution with hexanes 1.23 g (92% yield) of a 1:1.2 mixture of alkenes **24a,b** as a colorless liquid.

Alkene **24a:** ^{1}H NMR δ 7.3 (m, 2 H), 7.2 (m, 3 H), 5.17 (br t, J = 7.1 Hz, 1 H), 2.63 (t, J = 7.0 Hz, 2 H), 2.29 (dt, J = 7.1, 7.0 Hz, 2 H), 1.68 (s, 3 H), 1.56 (s, 3 H); ^{13}C NMR δ 142.4, 132.0, 128.4 (2 C), 128.2, 123.7, 37.3, 29.3, 25.6, 22.4; lit.[15a] no spectral data.

Alkene **24b:** ^{1}H NMR δ 7.3 (m, 2 H), 7.2 (m, 3 H), 4.72 (br s, 1 H), 4.69 (br s, 1 H), 2.57 (t, J = 6.5 Hz, 2 H), 2.05 (t, J = 7.3 Hz, 2 H), 1.75 (m, 2 H), 1.72 (s, 3 H); ^{13}C NMR δ 145.6, 142.5, 128.4 (2 C), 128.2, 110.0, 36.1, 35.5, 30.0, 17.6; lit.[37] no spectral data.

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(35) Morin, G. F.; Horton, W. J.; Grant, D. M.; Dalling, D. K.; Pugmire, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 3992–3998.

(36) (a) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1966**, *31*, 89–94. (b) Abdel-Wahab, A.-M. A.; Ismail, M. T.; Mohamed, O. S.; Khalaf, A. A. *Gazz. Chim. Ital.* **1985**, *115*, 591–594.

(37) Wolinsky, J.; Clark, G. W.; Thorstenson, P. C. *J. Org. Chem.* **1976**, *41*, 745–750.