as a light oil and was assigned as 2,5-dimethyl-3-phenylhex-2-en-4-one (**38**) on the basis of the following spectral characteristics: NMR (90 MHz, CCl$_4$) δ 0.9 (d, J = 7 Hz, 6 H), 1.65 (s, 3 H), 1.85 (s, 3 H), 2.45 (septet, J = 7 Hz, 1 H), and 7.03–7.45 (m, 5 H); IR (neat) 2975, 1685, 1600, 1490, 1445, 1380, 290, 1190, 1155, 1050, 1030, 930, 845, 775, 715 cm^{-1}; UV (cyclohexane) 237 nm (ϵ 8900), 243 nm (ϵ 8800), 248 nm (ϵ 8100), 254 (ϵ 6200), and 260 nm (ϵ 3800); MS, *m/e* 202 (M$^+$), 159, 131 (base), and 91. Anal. Calcd for C$_{14}$H$_{18}$O: C, 83.12; H, 8.97. Found: C, 82.89; H, 8.99.

A 0.85-g sample of 1-phenyl-2-(2-hydroxy-2-propyl)-3,3-dimethylcyclopropene (**35**) was stirred in 50 mL of dry tetrahydrofuran with 0.925 g of Burgess' reagent[29] and 0.6 mL of triethylamine at room temperature for 12 h. The crude mixture was concentrated under reduced pressure and the residue was taken up in ether and washed twice with water. The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was percolated through 2 × 10 cm of silica gel with hexane as the eluent. The major product contained 300 mg (38%) of a light yellow oil whose structure was identified as 1,1-dimethyl-3-phenyl-3-(2-propenyl)allene (**37**) on the basis of the following spectral properties: NMR (90 MHz, CCl$_4$) δ 1.75 (s, 6 H), 1.87 (s, 3 H), 4.78 (br s, 1 H), 4.95 (br s, 1 H), and 7.13–7.30 (m, 5 H); IR (neat) 2920, 1950, 1735, 1620, 1600, 1493, 1447, 1378, 1365, 1310, 1210, 1175, 1077, 1043, 1020, 973, 893, 765, 730, and 700 cm^{-1}.

A 200-mg sample of allene **37** was heated at reflux in 25 mL of dry benzene with 210 mg of *p*-toluenesulfonic acid for 15 min. The reaction was cooled, extracted with a saturated sodium bicarbonate solution, and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was percolated through 2 × 15 cm silica gel with a 5% acetone:hexane mixture as the eluent. The major product isolated contained 120 mg (30%) of a light oil which was identical in all respects with a sample of 2,5-dimethyl-4-phenyl-3-(*o*-tosyl)-2,4-hexadiene (**39**) which had been previously isolated.

A 130-mg sample of allene **37** was also heated at reflux in 25 mL of methanol with a few drops of concentrated sulfuric acid for 1 h. The reaction mixture was allowed to cool and was then concentrated under reduced pressure. The crude mixture was dissolved in ether, extracted with a saturated sodium bicarbonate solution, and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The major product contained 60 mg (42%) of a light oil whose structure was identical in all respects with a sample of 2,5-dimethyl-3-phenylhex-2-en-4-one (**38**).

Acknowledgment. We are grateful to the National Science Foundation for financial support. A.P. wishes to express his appreciation to the organic group at the University of Wurzburg for their cordial hospitality during his stay as a Senior Humboldt Awardee. Use of the high-field NMR spectrometer used in these studies was made possible through a NSF equipment grant.

Registry No. **3**, 21603-24-7; **4**, 83831-84-9; **5**, 83831-85-0; **6**, 83831-86-1; **7**, 83831-87-2; **10**, 92421-07-3; **11**, 92421-11-9; **12**, 92421-09-5; **14**, 92421-06-2; **15**, 92421-08-4; **16**, 92421-10-8; **17**, 92421-12-0; **24**, 92421-13-1; **25**, 92421-15-3; **26**, 92421-14-2; **31**, 92421-16-4; **32**, 92421-17-5; **33**, 15958-02-8; **34**, 7476-41-7; **35**, 92421-18-6; **37**, 92421-21-1; **38**, 92421-20-0; **39**, 92421-19-7; (1,1-dimethylphenyl)propargyl alcohol, 1719-19-3; (1,1-dimethylphenyl)propargyl bromide, 75111-04-5; 2-bromopropene, 557-93-7; phenylacetylene, 536-74-3; methyl phenylpropiolate, 4891-38-7.

Supplementary Material Available: Table of fractional coordinates for non-hydrogen atoms of 1,4-dicarbomethoxy-2,2-dimethyl-3-phenyl-4-(1-phenyl-2-methylprop-1-enyl)bicyclo[1.1.0]butane (4) (4 pages). Ordering information is given on any current masthead page.

Use of Solid Acids To Catalyze the Cis/Trans Photoisomerization of α,β-Unsaturated Carbonyl Compounds[1]

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The cis/trans isomerization of solutions of ethyl cinnamates, **1** and **2**, 4-phenylbut-3-en-2-ones, **3** and **4**, and cinnamonitriles, **5** and **6**, has been examined in the presence of heterogeneous acids such as the aluminosilicates and Nafion. The proportion of the cis isomer present in the photostationary-state mixtures of **1** and **2** and **3** and **4** is dramatically enhanced when heterogeneous acids are present, a finding that is of preparative significance. The origin of this type of perturbation of the photostationary states of unsaturated esters and ketones has been examined in detail and it is shown that the primary factor involved is the preferential adsorption of the trans vs. the cis isomers.

The photoinduced cis/trans isomerization of olefins is a ubiquitous reaction that is of considerable use in the preparation of the thermodynamically less stable cis isomers.[3] One detrimental feature of these reactions from a preparative point of view is that the photostationary states reached frequently contain approximately equal amounts of both isomers and this necessitates separation and recycling steps. In 1981, Lewis and Oxman reported that the position of the photostationary states reached with α,β-unsaturated esters can be dramatically altered if a Lewis acid is present in the solution.[4] For example, irradiation of a benzene solution of ethyl cinnamate containing less than a molar equivalent of ethyl aluminum dichloride yielded a photostationary state containing 85% of the cis isomer. In the absence of the Lewis acid only 42% of the cis isomer was present at the photostationary state.

Recently an increasing amount of attention has been given to the use of surfaces to modify the course of a

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[2] On leave from the Technical University of Wroclaw, Poland.

[3] Saltiel, J.; Charlton, J. L. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 25–89.

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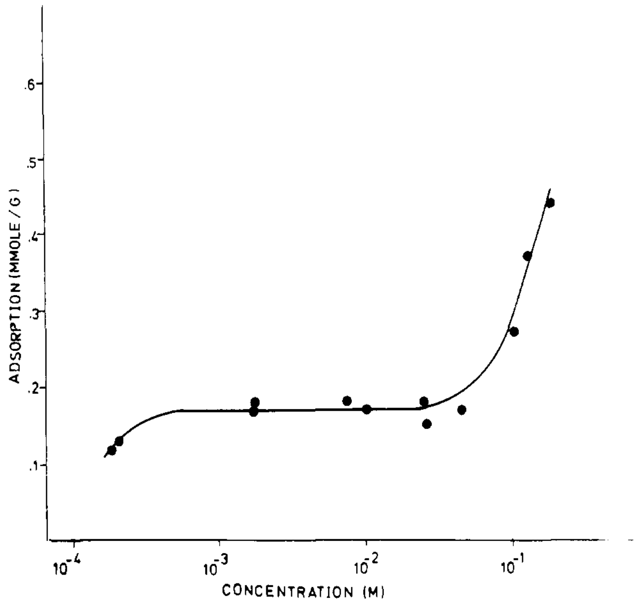


Figure 1. Adsorption of 1 on Al_2O_3/SiO_2 as a function of concentration in solution.

photochemical reaction.[5] In this context we have been examining the use of solid acids to catalyze the photoreactions of organic materials.[6] The ease of removal of such an acid from a solution and the possibility of using a continuous flow type photoreactor make such acids particularly promising in terms of preparative photochemistry. In this paper we show that aluminosilicates can perturb the photoreactions of ethyl cinnamate and 4-phenyl-but-3-en-2-one and enhance the proportion of the cis isomer reacted at the photostationary state. These reactions appear to involve oxygen coordinated or protonated species adsorbed on the acidic surface. In addition it is shown that a solid Brønsted acid such as Nafion in its acid form can also serve as an effective catalyst. The origin of this catalysis is discussed.

Results and Discussion

Aluminosilicates as Catalysts. Aluminosilicates are strongly acidic materials which possess both Brønsted and Lewis acid sites.[7] On the other hand unsaturated carbonyl compounds such as the cinnamates are relatively basic materials[8] which would be expected to be strongly adsorbed on an activated aluminosilicate.

The adsorption of 1 and 2 from anhydrous CH_2Cl_2 onto the aluminosilicate (12% Al_2O_3) was examined quantitatively. Typical results are shown in Figure 1 for the adsorption of 1. With concentrations of 1 in the contacting solution in the 10^{-3} to 5×10^{-2} M range the amount of ester adsorbed remained essentially constant at 0.17 mmol adsorbed/g of catalyst. At higher concentrations there was a rapid increase in the amount of ester adsorbed. This type of behavior suggests that monolayer coverage is occurring up to the 5×10^{-2} M breakpoint.[9] The cis ester 2 exhibited exactly comparable behavior of 1 although it was less strongly adsorbed.

Table I. UV Data

no.	solvent	acid	λ_{max}	log ϵ
1	CH_2Cl_2		277	4.35
	CH_2Cl_2	$AlEtCl_2$	328	4.46
	C_6H_6	Al_2O_3/SiO_2	320	
	FSO_3H	FSO_3H	328	4.30
2	CH_2Cl_2		269	4.03
	CH_2Cl_2	$AlEtCl_2$	328	4.05
3	CH_2Cl_2		286	4.51
	CH_2Cl_2	$AlEtCl_2$	372	4.69
	FSO_3H	FSO_3H	370	4.76
	C_6H_6	$Al_2O_3{\cdot}SiO_2$	330	
4	CH_2Cl_2		281	4.18
	CH_2Cl_2	$AlEtCl_2$	372	4.57
5	CH_2Cl_2		275	4.41
	CH_2Cl_2	$AlEtCl_2$	315	4.47
	C_6H_6	Al_2O_3/SiO_2	310	
	FSO_3H	FSO_3H	317	4.48
6	CH_2Cl_2		275	4.25
	CH_2Cl_2	$AlEtCl_2$	322	4.08

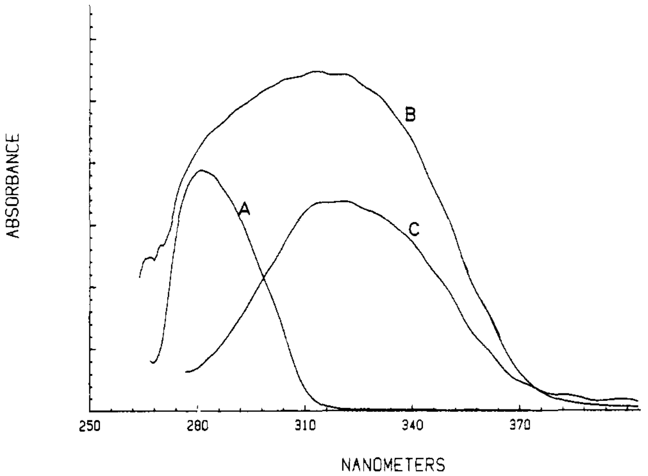
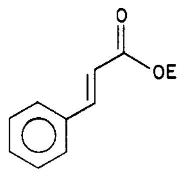


Figure 2. UV spectra of 1 in C_6H_6 (A), of 1 in C_6H_6 in the presence of Al_2O_3/SiO_2 (B), and of 1 adsorbed on Al_2O_3/SiO_2 obtained by subtraction of A from B (C).



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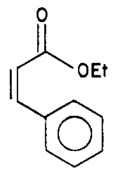

2

In order to characterize the nature of the adsorbed esters the UV spectra of these systems and some model compounds were examined. The neutral esters 1 and 2 in solution exhibit strong absorption maxima at 277 and 269 nm, respectively. Dissolution of 1 and 2 in FSO_3H at low temperatures leads to the formation of **1H** and **2H** which were characterized by ^1H NMR spectroscopy, Table II. The Lewis acid complexes of 1 and 2 were formed in dry CH_2Cl_2 using a variety of Lewis acids and again the adducts were characterized by their ^1H NMR spectra, Table II. The $SnCl_4$ and $AlEtCl_2$ complexes of 2 were thermally stable at ambient temperatures while **2SbCl$_5$** reverted to **1SbCl$_5$** under these conditions.[10] As can be seen from the

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Table II. ^1H NMR Data for α,β-Unsaturated Compounds

				chemical shift,[a,b] ppm				coupling constant, Hz
no.	Lewis acid[c]	solvent	temp, °C	H_2	H_3	aryl H	other	$J_{2,3}$
1		CD_2Cl_2	35	6.45 d	7.63 d	7.3–7.6 m	4.27 q, 1.35 t	16.1
1		FSO_3H	35	6.87 d	8.62 d	7.5–8.1 m	5.03 q, 1.73 t	16
1	$AlCl_2Et$[d]	CD_2Cl_2	35	6.90 d	8.21 d	7.5–7.7 m	4.7 bq, 1.5 bt	15.7
				6.88 d	8.29 d			15.8
1	$SbCl_5$	CD_2Cl_2	-70	6.42 d	8.15 d	7.3–7.6 m	4.66 q, 1.50 t	15.8
1	$SnCl_4$	CD_2Cl_2	35	6.83 d	7.94 d	7.3–7.6 m	4.48 q, 1.43 t	15.9
2		CD_2Cl_2	35	5.90 d	6.95 d	7.3–7.6 m	4.14 q, 1.23 t	12.6
2		FSO_3H	-70	6.40 d		7.5–8.1 m	4.9 bq, 1.5 bt	12
2	$AlCl_2Et$	CD_2Cl_2	35	6.41 d	7.70 d	7.5–7.7 m	4.54 q, 1.24 t	12.2
2	$SbCl_5$	CD_2Cl_2	-70	6.77 d	7.69 d	7.3–7.6 m	4.52 q, 1.34 t	12.2
2	$SnCl_4$	CD_2Cl_2	35	6.15 d	7.19 d	7.3–7.6 m	4.25 q, 1.20 t	12.4
3		CD_2Cl_2	35	6.75 d	7.58 d	7.3–7.6 m	2.40 s	16.2
3	$SnCl_4$	CD_2Cl_2	35	7.10 d	8.01 d	7.4–7.8 m	2.77 s	16.0
4		CD_2Cl_2	35	6.19 d	6.93 d	7.3–7.6 m	2.19 s	12.7
4	$SnCl_4$	CD_2Cl_2	35	6.46 d		7.4–7.8 m	2.56 s	12.1
5		CD_2Cl_2	35	5.92 d	7.43 d	7.3–7.5 m		16.7
5	$SnCl_4$	CD_2Cl_2	35	6.02 d	7.65 d	7.4–7.5 m		16.7
6		CD_2Cl_2	35	5.48 d	7.17 d	7.3–7.5 m		12.2
6	$SnCl_4$	CD_2Cl_2	35	5.59 d		7.4–7.5 m		12.2

[a] In ppm from CH_2Cl_2 (5.421, -70 °C; 5.336, +35 °C). [b] d = doublet, m = multiplet, q = quartet, bq = broad quartet, t = triplet, bt = broad triplet. [c] 1.1–1.2 M equiv of acid were used, concentration = 0.2–0.3 M. [d] In the case of 1 with 1.2 M equiv of $AlCl_2Et$, two sets of signals for the ester were observed, indicating the occurrance of disproportionation (ref 17).

data presented in Table I, both the protonated and complexed forms of 1 and 2 exhibited very similar UV spectra with strong absorption maxima at 328 nm.

The adsorption of 1 on dried aluminosilicate powder was followed by UV spectroscopy. Under conditions where less than a monolayer coverage occurred, a new absorption band was observed at 320 nm, Figure 2. With unactivated aluminosilicate catalyst only minor changes in the UV spectrum of ethyl cinnamate were observed and no new absorption bands were formed. Changes in the UV spectrum of the magnitude seen above with the dried catalyst and the similarity of the position of the absorption maximum to that observed in homogeneous solution for the fully protonated or complexed ester strongly suggests that the carbonyl oxygen of the adsorbed ethyl cinnamate is either protonated or complexed with a surface acid site on the catalyst.

No thermally induced cis to trans isomerizations of 2 to 1 were observed when solutions of 2 were left in contact with the catalyst for several days at room temperature.

Photoisomerizations. The photoreactions were carried out in one of two ways. In the first method a CH_2Cl_2 solution of the ester was continuously passed through beds of the catalyst packed in narrow Pyrex tubes. These tubes were irradiated using a Rayonet photoreactor and 300-nm lamps with care being taken to shield the bulk of the solution from the light. The reactions were carried out under nitrogen or argon with the exclusion of moisture. Comparable conversions were obtained more simply by placing the powdered aluminosilicate or Nafion beads in a test tube together with a solution of the ester and stirring the suspension with a magnetic stirrer. By using black tape around the top of the tube it was possible to restrict the incident light to the part of the tube containing the catalyst slurry. All of the photochemical experiments were carried out with a Pyrex filter, cutoff 300 nm, in order to maximize the fraction of the incident light which is absorbed by protonated or complexed species.

Under either of these conditions, the composition of the cinnamates in the CH_2Cl_2 solution in contact with the aluminosilicate was monitored as a function of irradiation time and the overall concentration of the solutions. In each case a photochemical cis/trans isomerization was observed and a photostationary state was reached. As can be seen from Figure 3, the final composition of solution was dependent upon the total ester concentration. The maximum conversion achieved was to a mixture containing 85% cis, 15% trans ethyl cinnamate with total ester concentrations below 10^{-2} M. Above this concentration there was a fairly abrupt decrease in the proportion of the cis isomer obtained. This fall off at concentrations greater than 10^{-2} M corresponds approximately with the onset of a rapid increase in the amount of ester adsorbed on the catalyst as noted in the experiments described above.

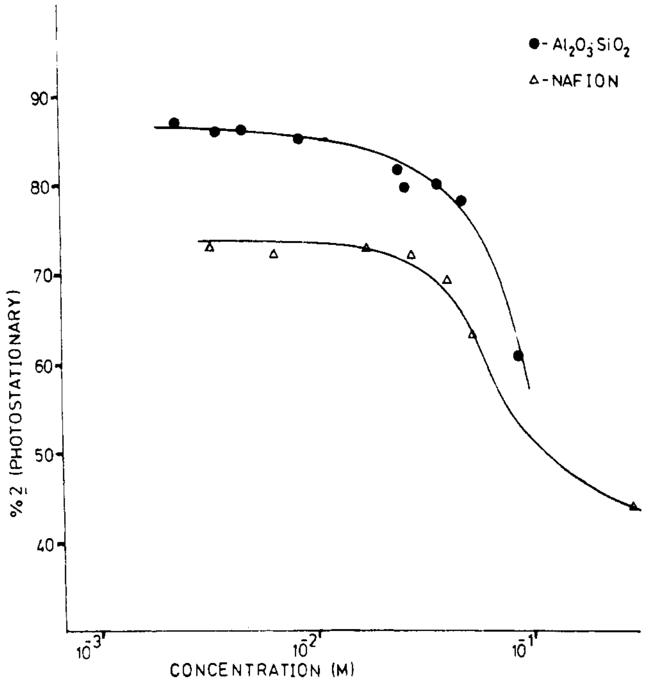


Figure 3. Composition of photostationary state reached on irradiation of solutions of 1 in presence of Al_2O_3/SiO_2 and Nafion.

The composition of and amounts of the esters remaining adsorbed by the catalyst were examined. The adsorbed esters were recovered by treatment of the aluminosilicate with methanol. The composition of the adsorbed material varied somewhat from run to run, but was typically in the 50–60% cis, 40–50% trans range. The total material balance was good with typically less than a 5% loss in the

Table III. Typical Irradiation of *trans*-Ethyl Cinnamate

catalyst (SiO_2/Al_2O_3): 4.9551 g
solution (CH_2Cl_2): 50 mL of 0.06122 M in trans isomer
irradiation: 40 h (Rayonet Photochemical Reactor 300 nm)
composition of resulting solution: 77.9% cis, 22.1% trans
concentration of trans isomer: 0.01012 M
concentration of cis isomer: 0.03557 M
desorption of adsorbed material; recovered:
  cis-ethyl cinnamate 0.4673 mol 59.3%
  trans-ethyl cinnamate 0.3205 mmol 40.7%
total material balance
  initial: 0.00306 mol of trans isomer
  resulting solution: 0.00228 mol (cis and trans isomers)
  adsorbed on catalyst: 0.000788 mol (cis and trans isomers)
  total material accounted for after reaction: 0.00307 moles

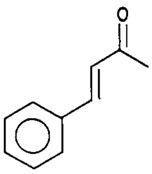
total amount of ester used. Details of a typical experiment are given in Table III.

After removal of the solution from a particular catalyst it was possible to reuse the aluminosilicate for subsequent photochemical reaction. Comparable limiting conversions of **1** to **2** were reached in this second reaction as were achieved in the first.

It should be stressed that the photostationary-state compositions reached in these experiments with the aluminosilicate are much different from the 42:58 ratio of **2**:**1** established in the absence of the catalyst. Clearly the presence of the aluminosilicate surface is modifying the course of the photoreactions. It is interesting that the limiting composition of the solution (85% of the cis isomer) is the same as that reported by Lewis and Oxman for the comparable homogeneous reaction involving $[AlEtCl_2]_2$ as a catalyst.[4]

Extension to Other Systems. The catalyzed photoisomerizations of the ketones **3** and **4**, and nitriles **5** and **6**, were also examined. The protonated and Lewis acid complexed forms of these systems were formed by dissolution in FSO_3H at low temperatures or by reaction with a variety of Lewis acids in dry CH_2Cl_2. In each case the conjugate acid or Lewis acid adduct was characterized by UV and ^1H NMR spectroscopy, Tables I and II. Both **4H** and **4AlEtCl$_2$** thermally isomerized to **3H** and **3AlEtCl$_2$**, respectively, at 25 °C.

The adsorption of **3** and **5** on the aluminosilicate catalyst was followed spectroscopically and the results are summarized in Table I. In the case of **5** it would again seem that protonated or complexed species are being formed. The spectral shift observed with **3** is substantially less than is observed in homogeneous solutions on protonation or complexation and it is not clear as to the exact nature of the adsorbed species. Thermal control experiments showed that **4** isomerized to **3** at room temperature when in the presence of the activated catalyst and it was necessary to carry out irradiations of **3** at low temperatures.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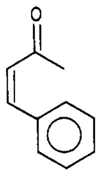
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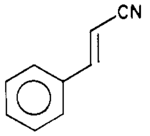
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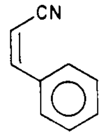
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Irradiation of **3** in the absence of the catalyst led to the formation of a photostationary-state mixture containing 52% **4**, 48% **3**. With a 5 × 10^{-3} solution of **3** in contact with the aluminosilicate, the limiting conversion achieved was to a mixture consisting of 81% **4** and 19% **3**. Thus **3** and **4** are behaving in a very similar manner to **1** and **2**, suggesting that protonated or complexed species are involved in these reactions. In contrast, in the case of **5** and **6** no change was observed in the photostationary state when the irradiations were carried out in the presence of an aluminosilicate, Table IV.

Table IV. Summary of Photostationary-States Compositions

system	catalyst	solvent	total concentration, M	composition	
				cis, %	trans, %
1/2		CH_2Cl_2	0.2	42	58
1/2	aluminosilicate	CH_2Cl_2	1 × 10^{-2}	85	15
1/2	Nafion H	CH_2Cl_2	1 × 10^{-2}	73	27
3/4		CH_3Cl_2	0.2	52	48
3/4	aluminosilicate	CH_2Cl_2	5 × 10^{-3}	81	19
5/6		CH_2Cl_2	0.2	66	34
5/6	aluminosilicate	CH_2Cl_2	5 × 10^{-3}	66	34
1H/2H		FSO_3H	0.2	39	61
1AlEtCl$_2$/2AlEtCl$_2$		CH_2Cl_2	0.2	58	42

Nafion as a Photocatalyst. Nafion is a perfluorinated acid resin containing sulfonic acid groups located on $-(OCF_2CF(CF_3))_n-OCF_2CF_2SO_3H$ side chains attached to a perfluorocarbon backbones. The dried, CH_2Cl_2 swollen Nafion used in this work was found to have an H_0 value of about −6.[11]

The adsorption of **1** from dry CH_2Cl_2 onto Nafion-125 membrane was examined by UV spectroscopy and the formation of a strong absorption band at 330 nm was observed. This band corresponds closely with that of the fully protonated ester, **1H**, in FSO_3H, Table I.

Irradiation of CH_2Cl_2 solutions of **1** in the presence of Nafion-501 beads led to the formation of photostationary-state mixtures of **1** and **2** which had a greater proportion of **2** than could be obtained without the use of the catalyst. The photostationary-state compositions were dependent on the concentration of the solution contacting the Nafion, Figure 3. The limiting composition reached was 73% of the cis isomer with concentrations of **1** and **2** in the contacting solution of less than 1 × 10^{-2} M. A fall off in the amount of cis isomer present at the photostationary-state mixtures was observed as the total ester concentration exceeded 10^{-2} M.

Basis of Catalysis. In their original communication Lewis and Oxman suggested that the change in photostationary-state composition attendant upon addition of a Lewis acid to unsaturated esters was due to a combination of change in the extinction coefficients and quantum efficiencies for the interconversion of the complexed vs. the free esters.[4] The compositions observed could seemingly be accounted for using eq 1 and the appropriate

$$\frac{[\text{cis}]}{[\text{trans}]} = \frac{\phi_{\text{t-c}},\ \epsilon_{\text{t}}}{\phi_{\text{c-t}},\ \epsilon_{\text{c}}} \qquad (1)$$

data for the complexed esters. Thus ethyl cinnamate in the presence of $AlEtCl_2$ would be expected to lead to a photostationary state containing 83% of the cis and 17%

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[11] Measurements on the acidity of the Nafion used in this work indicate an H_0 = −6.5. Nafion is expected to be more acidic than this. Olah, G. A.; Prakash, G. K. S.; Summer, J. *Science* **1979**, *206*, 13–20.

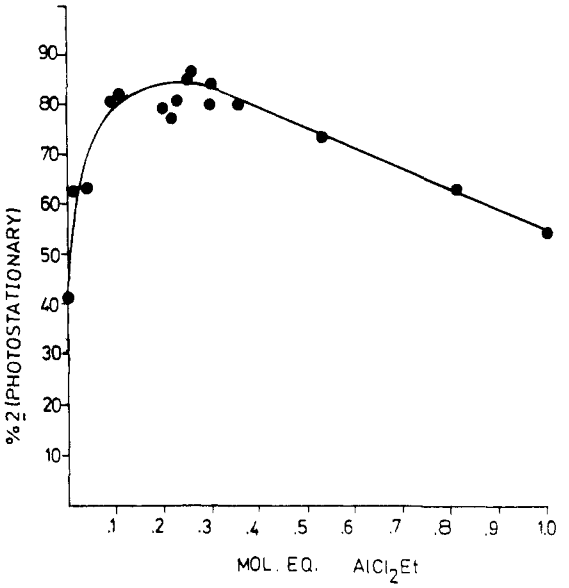

Figure 4. Composition of photostationary state reached on irradiation of CH_2Cl_2 solutions of **1** in presence of varying amounts of $[AlEtCl_2]_2$.

of the trans isomers using the data for the fully complexed esters. This compares favorably with a measured value of 85% cis and 15% trans.

While the agreement between calculated and observed compositions is reasonably good, the result obtained above with Nafion caused us to question this explanation. Nafion is exclusively a Brønsted acid and thus only protonated esters would be involved. Our past experience with the photoisomerization of protonated unsaturated esters and other related carbonyl compounds showed that while these systems underwent efficient cis/trans isomerizations, the photostationary-state compositions were typically not far removed from those encountered for the corresponding esters themselves.[12] To check this point the photoisomerization of fully protonated ethyl cinnamate was examined. Irradiation of a FSO_3H solution of **1H** at -60 °C in order to prevent this unwanted thermal reversion, led to the formation of a photostationary state with 39% **2H** and 61% **1H**. This photostationary-state composition is completely different from the results obtained with the Nafion. It is difficult to account for such a large discrepency in the photostationary-state compositions in the Nafion and FSO_3H reactions simply on the basis of the difference in temperature of the two reactions.[13]

As a further check the composition of the photostationary state with fully complexed esters was examined. Irradiation of a CH_2Cl_2 solution of ethyl cinnamate containing a molar excess of $[EtAlCl_2]_2$, under conditions where all the ester was complexed, led to the formation of a photostationary state with 58% **2AlEtCl$_2$** and 42% **1AlEtCl$_2$**. It is clear that the origin of the catalytic effect of the heterogeneous acids presented above and the solution results of Lewis and Oxman can not be accounted for on the basis of a simple application of eq 1. This point is emphasized by a consideration of the data summarized in Figure 4 in which the photostationary-state composition is shown to vary significantly as a function of the molar ratio of Lewis acid to ester used.

Scheme I

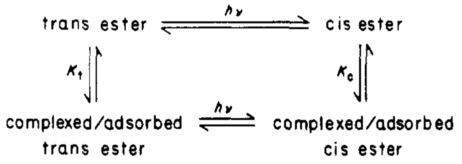

Table V. Ratio of Equilibrium Constants for Complex Formation

system	Lewis acid	temp, °C	K_t/K_c[a]
1/2	$AlEtCl_2$	35	7 ∓ 1
	$SnCl_4$	35	$3.1 \mp .5$
	$SbCl_5$	-60	11 ∓ 1
3/4	$SnCl_4$	35	$4.7 \mp .5$
5/6	$SnCl_4$	35	$0.95 \mp .5$

[a] K_t = [complex]/[Lewis acid][trans base]. K_c = [complex]/[Lewis acid][cis base].

In the case of the solid acids described here and also the homogeneous acids of Lewis and Oxman, enhanced production of the cis isomer occurs when there is a molar deficiency of the Lewis acid present. As such there are four species present in solution, cis and trans ethyl cinnamate and complexed or adsorbed esters, Scheme I.

While the magnitudes of the two equilibrium constants, K_t and K_c, in Scheme I will be large with the esters and the strong Lewis and Brønsted acids used in this work, they need not be of the same size. Indeed the pK_{BH^+} values of the analogous protonated cinnamic acids are known to be different with the cis isomer being a stronger acid than the trans.[14] The ratio of K_t/K_c was measured with $[AlEtCl_2]_2$, $SnCl_4$, and $SbCl_5$ in CH_2Cl_2 using ^1H NMR techniques. At room temperature where there was a rapid exchange between free and complexed esters with the former Lewis acid, the degree of complexation was determined by measuring the averaged chemical shift and comparing this with chemical shifts of the free and fully complexed esters. Starting with a molar deficiency of $[AlEtCl_2]_2$ and a mixture of the cis and trans isomers, the ratio of K_t/K_c for ethyl cinnamate was found to be 7 ∓ 1 at 35 °C.[15] A similar measurement with $SnCl_4$ as the Lewis acid gave a smaller value. With $SbCl_5$ the thermal reversion of **2SbCl$_5$** to **1SbCl$_5$** meant that the measurement of K_t/K_c had to be carried out at low temperatures on nonexchanging spectra. Similar measurements were carried out with the ketones **3** and **4** and nitriles **5** and **6**, Table V. In the case of **3** and **4** alkylation reactions were encountered when $[AlEtCl_2]_2$ was used as the Lewis acid and poor solubility of the $SbCl_5$ complexes precluded quantitative measurements with these Lewis acids.

It is clear from the measurements of K_t/K_c that in the case of both the esters and ketones the trans compounds bind more strongly with the Lewis acids than the corresponding cis compounds. These differences probably arise from steric effects in the cis compounds which make it more difficult for the unsaturated systems to be completely planar, thus reducing their basicity relative to the planar trans compounds. This effect would be absent in the

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[12] Childs, R. F.; Lund, E. F.; Marshall, A. G.; Morrisey, W. J.; Rogerson, C. V. *J. Am. Chem. Soc.* **1976**, *98*, 5924-5931.

[13] Some temperature dependence on the quantum efficiencies for the two photoreactions might be expected and a modest temperature dependence of the photostationary state could occur. Childs, R. F.; Cochrane, A. W. *J. Org. Chem.* **1981**, *46*, 1086-1089.

[14] Noyce, D. S.; King, P. A.; Kirby, F. B.; Reed, W. L. *J. Am. Chem. Soc.* **1962**, *84*, 1632-1635.

[15] Complexation of $[AlEtCl_2]_2$ with carbonyl compounds is a complex reaction involving disproportionation and reproportionation of the Lewis acid.[16] Under the fast exchange conditions used here the various different types of complex which will be formed could not be detected. At low temperatures these solutions showed at least two complexes to be present for each of the cis and trans esters.

[16] Nixon, A.; Childs, R. F. *J. Polym. Sci. Polym. Chem. Ed.* **1980**, *18*, 1499-1509.

nitriles **5** and **6**, and indeed K_t/K_c for these compounds is very close to 1. The variation of K_t/K_c with Lewis acid has not been explored with a sufficiently large series of compounds and acids for trends to become apparent. It should be remembered, however, that Lewis acids such as $SnCl_4$ can bind to more than one Lewis base,[4a] and steric effects at the Lewis acid site can not be ignored when comparisons between different acids are made.

Returning to the photochemical reactions it is now evident why the presence of a Lewis acid can have a pronounced effect on the photostationary state reached with the esters and ketones but not the nitriles. As all the irradiations were carried out through Pyrex, most of the incident light will be absorbed by the complexed or adsorbed species. For example, with equal concentrations of complexed and free *cis*- and *trans*-ethyl cinnamates in solution, some 96% of the light above 300 nm would be absorbed by the complexed esters (Table I). The effect of the irradiation would be to establish a photostationary state between the complexed esters and consequently modify the composition of the free esters by exchange. A similar situation pertains with the heterogeneous acids.

Assuming all the light is absorbed by the complexed or adsorbed esters then the ultimate composition of the free esters in equilibrium with the complexed esters should be given by eq 2 where CC and TC are the photostationary-state concentrations of the cis and trans complexes, respectively.

$$\frac{[\mathrm{cis}]}{[\mathrm{trans}]} = \frac{K_t[\mathrm{CC}]}{K_c[\mathrm{TC}]} \tag{2}$$

Substituting the appropriate values for ethyl cinnamate/$[AlEtCl_2]_2$ into eq 2, a cis/trans ratio of the free esters in equilibrium with photostationary-state mixture of the complexed esters would be expected to be about 9.6/1 or 90% of the cis isomer. This is not far removed from the compositions achieved by using catalytic amounts of Lewis acid or the aluminosilicate.

In this context it is worth noting that the composition of the cinnamates adsorbed on the aluminosilicate after irradiation were close to that expected for a photostationary-state mixture of fully complexed esters. This supports the analysis of the origin of the effect given above and also reinforces the suggestion that with the concentrations used here with this catalyst, the adsorbed esters are oxygen complexed.

Overall this type of photocatalysis derives from a series of factors. These include chromophore modification on complexation or adsorption, the resultant change in extinction coefficients of free and bound organic substrate at the irradiation wavelength, and modification of the quantum yields for the photoreaction as discussed by Lewis and Oxman.[17] Most importantly, however, is the selective complexation or adsorption of the starting material by the hetero- or homogeneous Lewis acid. This approach to the modifications of the position of a photostationary state should be of general applicability wherever there is a difference in the equilibrium constants for the complexation of one of the isomers. Where no such difference exists, as for example in the case of the nitriles **5** and **6** in this work, complexation or the presence of a heterogeneous acid will only alter the photostationary state if the relative magnitude of the various extinction coefficients and quantum efficiencies are altered on complexation.

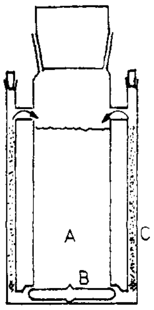

Figure 5. Photochemical apparatus. (A) Central reservoir with opaque walls containing solution of substrate. (B) Magnetic stirrer bar which forces solution up through four cylindrical tubes. (C) Containing the powdered catalyst which are irradiated with an external light source.

In conclusion we have shown here that heterogeneous acid catalysts can conveniently be used to modify the photostationary state reached in the photoisomerization of α,β-unsaturated carbonyl compounds. Removal of the heterogeneous catalyst from the organic compounds is simple, and indeed it is easy to conceive how a continuous flow reactor system could be set up, these heterogeneous acids providing a practical and cheaper alternative to the use of homogeneous solutions of Lewis acids. It would seem that the aluminosilicates are better catalysts than Nafion for these reactions. While the present study has only looked at the cis trans isomerization of unsaturated systems there is no reason why this type of catalysis could not be generally applicable to any other system in which a photostationary state is established and the materials have different affinities for a Lewis acid.

Experimental Section

General Methods. ^1H NMR spectra were obtained by using Bruker WM-250 or Varian EM-390 instruments. Gas chromatographic analyses were performed on a Hewlett-Packard 5790A gas chromatograph with a column containing 2% OV-101 on Chromosorb W. Preparative gas chromatography was performed on an Aerograph A-90-P3 instrument by using a column with 15% SE30 on Chromosorb W. UV spectra were measured on a Tracor Northern DARSS system or Pye Unicam instruments. The spectra of the adsorbed species on the Al_2O_3/SiO_2 were obtained by using transmittance spectra with finely powdered catalyst and benzene as a solvent. The spectra of adsorbed materials were obtained by subtraction of the spectrum of **1** in benzene from the initial spectrum.

Ethyl *cis*-cinnamate, **2**, and *cis*-4-phenyl-2-buten-3-one, **4**, were obtained by photoisomerization of **1** and **3**, respectively, by using the method of Lewis and Oxman.[4a] *cis*-Cinnamonitrile, **6**, was generated photochemically from **5** by irradiation in CH_2Cl_2 solution. Each of these compounds was purified by preparative GC and stored in sealed containers.

Protonations of compounds **1**–**6** were carried out by dissolution of the substrate in FSO_3H at −78 °C. The Lewis acid complexes of these materials were prepared by using a SMI digital micropipet which was calibrated by weight. All manipulations were carried out in a nitrogen glove box. CH_2Cl_2 was used as solvent for these complexes and was dried by standard procedures.[18]

Irradiations were carried out by using a Rayonet Photreactor (Southern New England Ultra-violet Company) with RPR 3000 Å lamps. Pyrex glass reactors were used throughout this work.

Acid Catalysts. Aluminosilicate pellets (Strem Chemicals) containing 12% Al_2O_3 were dried in a vacuum at 300 °C for 24 h. For some of the photochemical and UV experiments the pellets were powdered before drying. Nafion was conditioned and dried as previously described.[6]

Adsorption studies were carried out by using weighed samples of the dried SiO_2/Al_2O_0 catalyst and varying amounts of **1** in dried

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[17] From discussions with F. D. Lewis and J. D. Oxman it appears that they too have recognized the differential complexation as proposed in this paper is important in this type of Lewis acid catalysis.

[18] Jones, D. E. H.; Wood, J. L. *J. Chem. Soc. A* **1966**, 1448–1453.

CH_2Cl_2. The uptake of 1 was followed by either measuring the UV spectra of the solutions or by analytical GC with benzophenone as an internal standard. The adsorption was followed until no further change in concentration was observed. Typically adsorption was complete in less than 24 h. The results are given in Figure 1.

Desorption. The composition of the adsorbed esters after irradiation was determined by treating the CH_2Cl_2 washed catalyst with methanol. The methanol solutions were concentrated and analyzed by GC with benzophenone as an internal standard.

Photoisomerization with Solid Catalysts. All reactions were carried out under a nitrogen atmosphere with conditions which maximized light falling on the catalyst and minimized irradiation of the solutions. (A) The outside limbs of the reactor shown in Figure 5 were packed with ground SiO_2/Al_2O_3 (10–20 mesh) or Nafion pellets. A CH_2Cl_2 solution of 1 was added to the central compartment of the reactor which was covered with black tape. The solution was stirred with a magnetic stirrer. The effect of the stirrer was to force the solution up through the external tubes and return it to the top of the central reservoir. The outside limbs were irradiated in the Rayonet reactor and the reactions followed by removing aliquots for GC analysis. (B) The ground SiO_2/Al_2O_3 (0.5 g) or Nafion pellets, solvent (30 mL), and substrate (30 mg) were placed in a stoppered test tube (100 mL) and stirred with a magnetic stirrer. The stirring rate was adjusted so that a suspension of the catalyst was maintained in the bottom 3–4 cm of the tube. The upper portion of the tube was covered with black tape to minimise light adsorption by the substrate in solution in the absence of the catalyst. The course of the reactions was followed by GC analysis with benzophenone as an internal standard.

Registry No. **1**, 4192-77-2; **2**, 4610-69-9; **3**, 1896-62-4; **4**, 937-53-1; **5**, 1885-38-7; **6**, 24840-05-9; Nafion, 39464-59-0.

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^{13}C and ^{1}H Chemical Shift Assignments and ^{1}H–^{19}F Spin–Spin Coupling Constants in Oligosaccharides and Fluorinated Oligosaccharides by Two-Dimensional ^{13}C–^{1}H Chemical Shift Correlation Spectroscopy with Proton Homonuclear Decoupling

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A version of the two-dimensional ^{13}C–^{1}H chemical shift correlation NMR spectroscopy which includes selective spin flip pulses has been used to resolve and assign ^{1}H and ^{13}C chemical shifts and to determine ^{1}H–^{19}F spin–spin couplings of a series of oligosaccharides and fluorinated oligosaccharides. The selective spin flip results in almost complete homonuclear decoupling in the ^{1}H dimension, leading to substantially better resolution and signal to noise ratio.

Two-dimensional (2-D) ^{13}C–^{1}H chemical shift correlation NMR spectroscopy has become in the last few years a powerful and indispensable technique in making complete proton and ^{13}C NMR assignments of complex molecules.[1-4] Recently a new pulse sequence, which selectively flips the protons not directly bonded to the ^{13}C nucleus observed, has been proposed.[5-9] This pulse sequence has been incorporated into the ^{13}C–^{1}H chemical shift correlation technique,[8,9] resulting in the elimination of most of the ^{1}H–^{1}H homonuclear spin–spin couplings in the F_1 dimension. This new ^{13}C–^{1}H chemical shift correlation technique has now been applied to the study of a steroid (progesterone)[10] and a fluorinated steroid (9α-fluorocortisol).[11] The advantages of this new technique, as observed from these studies, are manifold. The peaks along the F_1 dimension are sharper, facilitating more accurate measurement of the ^{1}H chemical shifts as well as increasing the signal to noise ratio. In the case of CH_2 with nonequivalent protons, the geminal coupling between the two protons attached to the same carbon is not eliminated by this pulse sequence. Furthermore, an additional advantage of this technique is that it facilitates convenient measurement of the magnitude and relative sign of the couplings between ^{1}H and additional heteronuclei (e.g., ^{19}F, ^{31}P),[9,11] which normally are almost impossible to measure in complex molecules even by elaborate double-resonance techniques. Therefore, this method is most suitable for the study of complex molecules with additional heteronuclei.

The work of Hall and Morris[3,12] have demonstrated that ^{13}C–^{1}H chemical shift correlation is the most useful and reliable means of assigning the ^{13}C and especially the ^{1}H spectra of oligosaccharides.

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