carried out with the financial support of the ministry of Public Education (Rome).

Registry No. 1, 31452-21-8; 2, 40921-46-8; 3, 94500-16-0; 4, 94500-17-1; 5, 16648-23-0; 6, 94500-18-2; 7, 31452-22-9; CH_3SSCH_3, 624-92-0; $Me_3Sn\cdot$, 17272-57-0; $CH_3S\cdot$, 7175-75-9; $MeCH_2S\cdot$, 14836-22-7; $PrCH_2S\cdot$, 16812-18-3; $BrCH_2SCH_2CH_3$, 36056-14-1; $BrCH_2CH_2SCH_2CH_3$, 35420-95-2; $BrCH_2CH_2SBu$-*t*, 5755-60-2; $BrCH_2CH_2SBu$-*n*, 94500-19-3; ethyl disulfide, 110-81-6; ethylene, 74-85-1; cyclopropane, 75-19-4.

The Decomposition of Cumyl Peracetate on Silica

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The decomposition of cumyl peracetate follows heterolytic (Criegee), homolytic, or mixed heterolytic–homolytic pathways, depending on the polarity of the solvent and the presence of acid catalysts.[1,2] In acetic acid the rate (moderately fast at room temperature) and products (phenol, acetone, and 2-phenoxypropene) are characteristic of the heterolytic mode.[1] In nonpolar or moderately polar solvents such as toluene, the low rate (conveniently measured at 70 to 90 °C) and the products (mainly carbon dioxide, methane, and acetophenone, with lesser amounts of phenol, acetone, and 2-phenoxypropene) correspond to a mixed homolytic–heterolytic reaction.[2] The yield of 2-phenoxypropene is increased to 83% in the presence of trichloroacetic acid catalyst.[2]

In nonpolar solvents the decomposition rates are often erratic and difficult to reproduce, possibly because of reactions on the wall of the reaction vessel. The rate of the reaction in toluene in a Pyrex container is 40% greater when freshly crushed Pyrex is added.[2] It is also well-known that a number of reactions subject to homogeneous acid catalysis in solution are fast even on neutral silica. These observations impelled us to examine the perester decomposition on silica surfaces, with the object of identifying the heterogeneous part of the reaction.

Results

The rates of decomposition of the perester in silica slurries were too high to permit the removal of the solvent to confine the reaction to the adsorbed phase. With P_0 silica[3] the rate constant in a stirred chloroform slurry was 8.6×10^{-4} s^{-1} at 26 °C, which is faster than the extrapolated rate in toluene by 6 orders of magnitude and faster than the rate[1] in acetic acid by a factor of 30. The products from the reaction in a chloroform slurry of this silica were phenol (98% and 94%), acetic acid (89% and 92%), and acetone (88%). An IR band at 1763 cm^{-1}, probably due to the Criegee rearrangement product, 2-acetoxy-2-phenoxypropane, vanishes when the solution of reaction products is washed with water.

Similar experiments were carried out with slurries of P_1 silica.[3] Although the properties of P_1 silica as a medium for reactions confined to the surface, i.e., in the absence of liquid solvent, are often somewhat different from those of P_0 silica under the same solvent-free conditions,[4] the results from the two silicas appear to be the same in the present experiments.[8] The rate constant in a stirred chloroform slurry of P_1 silica at 26 °C was 9.6×10^{-4} s^{-1}. The products from the reaction in a pentane[5] slurry of P_1 silica were phenol (96%), acetic acid (89%), and acetone (91%).

Experimental Section

The chloroform slurry rates were determined from the carbonyl IR band of the perester in the supernatant liquid of samples of the slurry. The slurry was prepared from 50 mL of $CHCl_3$, 10.0 g of the silica, and 0.010 mol of the perester.

In a typical product determination, a solution of about 1 g of the perester in 25 mL of the solvent was added, with stirring, to a slurry of 25 g of the silica and 50 mL of the solvent. The slurry was filtered, products were removed from the silica by extraction with ether, and the ether combined with the filtrate. Phenol was determined by GLC using 4-methyl-2,6-di-*tert*-butylphenol as the internal standard and confirmed by isolation and weighing of the tribromophenol derivative. Acetic acid was determined by titration with alkali. Acetone was separated from the reaction mixture by distillation after neutralization of the acetic acid. The acetone in the distillate was determined gravimetrically as iodoform.

The perester was made from cumyl hydroperoxide and acetyl chloride as in ref 2. Iodimetric titration of this compound is not quantitative, but the preparation appeared to be pure as judged by its IR (carbonyl at 1785 cm^{-1}) and NMR: δ 1.65 (s, 6 H), 1.90 (s, 3 H), 7.40 (m, 5 H).

The Silicas.[4-7] The silicas were dried in an oven and stored over Drierite before use. Silica P_1 is the purer of the two and has 0.018% calcium as CaO, 0.005% iron as Fe_2O_3, 0.058% titanium as TiO_2, and 0.030% zirconium as ZrO_2. The percentages for P_0 silica are 0.02, 0.03, 0.09, and 0.03.[5] The surface areas (N_2) are 700 m^2/g for P_1 and 750 m^2/g for P_0. Silica P_1 has a greater H-bond donating ability, in the absence of solvent, as measured by its solvatochromic α value.[4] Both silicas have solvatochromic π^* values of about 2.0, greatly exceeding those reported for any fluid solvent.[4]

Registry No. Cumyl peracetate, 34236-39-0; silica, 7631-86-9.

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[8] The lack of dependence on the silica, P_0 vs. P_1, could be a result characteristic of this perester or it could be due to the presence of solvent. The fact that the products are the same in chloroform as in pentane supports the former interpretation.

Hydrogen–Deuterium Exchanges in a Friedel–Crafts Reaction

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Isotopic scramblings during Friedel–Crafts alkylations have been investigated with ^{14}C-labeled 2-arylethyl halides.[1] For example, scramblings in the 2-phenylethyl

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Table I. Data from Typical Mass Spectra in the Molecular Ion Region for 1,2-Diphenylethane (2) and Benzoic Acid (3)

molecular ions of 2[a]			molecular ions of 3[b]			molecular ions of 2[c]		
ion	m/z	rel abundance[d]	ion	m/z	rel abundance[e]	ion	m/z	rel abundance[f]
unlabeled 2	182	48.60	unlabeled 3	122	81.59	unlabeled 2	182	0.64
2-d_1 + 2-^{13}C	183	100.00	3-d_1 + 3-^{13}C	123	85.57	2-d_1 + 2-^{13}C	183	1.03
2-d_2 + 2-^{13}C-d_1	184	62.00	3-d_2 + 3-^{13}C-d_1	124	19.15	2-d_2 + 2-^{13}C-d_1	184	2.03
2-d_3 + 2-^{13}C-d_2	185	16.68	3-d_3 + 3-^{13}C-d_2	125	2.39	2-d_3 + 2-^{13}C-d_2	185	2.99
2-d_4 + 2-^{13}C-d_3	186	3.13	3-d_4 + 3-^{13}C-d_3	126	0.34	2-d_4 + 2-^{13}C-d_3	186	4.10
2-d_5 + 2-^{13}C-d_4	187	0.71				2-d_5 + 2-^{13}C-d_4	187	4.54
						2-d_6 + 2-^{13}C-d_5	188	3.96
						2-d_7 + 2-^{13}C-d_6	189	4.05
						2-d_8 + 2-^{13}C-d_7	190	6.67
						2-d_9 + 2-^{13}C-d_8	191	13.85
						2-d_{10} + 2-^{13}C-d_9	192	24.45
						2-d_{11} + 2-^{13}C-d_{10}	193	39.58
						2-d_{12} + 2-^{13}C-d_{11}	194	45.82
						2-d_{13} + 2-^{13}C-d_{12}	195	41.70
						2-d_{14} + 2-^{13}C-d_{13}	196	23.23
						2-^{13}C-d_{14}	197	7.92
							198	1.28
							199	0.61

[a] From reaction of 1-*1*-^{13}C-*2-Ph*-d_5 with benzene. [b] From oxidation of 2 from the reaction of 1-*1*-^{13}C-*2-Ph*-d_5 with benzene. [c] From reaction of 1-*1*-^{13}C with [$^2H_6$]benzene. [d] Base peaks with relative abundance of 100% also appear at m/z 91 and 92 for $C_7H_7^+$ and C_7H_7-$^{13}C^+$. [e] Base peak of 100% relative abundance appears at m/z 77 for $C_6H_5^+$. [f] Base peak of 100% relative abundance appears at m/z 97 for C_7H_7-d_6^+ + C_7H_7-^{13}C-d_5^+.

cation during the Friedel–Crafts alkylation of anisole[1a] or toluene[1b] with 2-phenyl[1-^{14}C]ethyl chloride (1-*1*-^{14}C) have been reported. In these cases, the aromatic moiety of the 2-arylethyl halide and the aromatic hydrocarbon had to be different in order for the Friedel–Crafts product, 1-*p*-anisyl-2-phenylethane or 1-phenyl-2-*p*-tolylethane, to be degraded to give benzoic acid and anisic or *p*-phthalic acid to allow for the observation of isotopic scrambling. Since we have recently made use of substrates doubly labeled with D and ^{13}C in solvolytic studies,[2] the possibility of investigating isotopic scramblings during the Friedel–Crafts reaction between 2-[$^2H_5$]phenyl[1-^{13}C]ethyl chloride (1-*1*-^{13}C-*2-Ph*-d_5) and benzene or between 2-phenyl[1-^{13}C]ethyl chloride (1-*1*-^{13}C) and [$^2H_6$]benzene was considered. Degradation of the isotopomeric 1,2-diphenylethane products to give various benzoic acids without or with the ^{13}C and/or Ph-d_5 label should give the extent of scrambling in the 2-phenylethyl cation during the Friedel–Crafts alkylation of benzene. It is anticipated that complications may arise since it is known that H–D or H–T exchanges can take place in aromatic compounds under acidic conditions.[3] However, it is of interest to determine the extent of such exchanges in a Friedel–Crafts reaction and if a limited and reproducible amount of H–D exchange were to occur, the rearrangement arising from 1,2-phenyl shifts during the Friedel–Crafts reaction between 1-*1*-^{13}C-*2-Ph*-d_5 and benzene or between 1-*1*-^{13}C and perdeuteriobenzene may still be observed.

When 1-*1*-^{13}C-*2-Ph*-d_5 was heated with an excess of benzene in the presence of $AlCl_3$ under conditions similar to those used for the alkylation of anisole with 1-*1*-^{14}C,[1a] 1,2-diphenylethane (2) was obtained in yields of about 40%. A typical set of mass spectral data in the molecular ion region of 2 is given in Table I, showing extensive loss of D presumably due to exchanges with the H atoms of benzene. Oxidation of this sample of 2 gave benzoic acid (3), the mass spectrum of which showed major peaks at m/z 122 and 123 for the molecular ions of unlabeled 3 and 3-^{13}C or 3-*d*, (Table I) but no peaks at m/z 127 and 128 for the molecular ions of C_6D_5COOH and $C_6D_5{}^{13}COOH$. Because of such extensive losses of D, an estimate of the amount of scrambling arising from 1,2-phenyl shifts was not feasible.

When the Friedel–Crafts reaction was carried out with 1-*1*-^{13}C and an excess of [$^2H_6$]benzene, the mass spectrum of the product, 2, again showed extensive H–D exchanges and the relative abundances for the various isotopomeric molecular ions for 2 are included in Table I. It is of interest to note that major peaks occur at m/z 192, 193, 194, 195 and 196, indicating some D incorporation into the aliphatic as well as the aromatic parts of 2. An appreciable amount of a molecular ion derived from a completely deuterated 2 containing both ^{13}C and 14 D atoms is also observed at m/z 197.

Thus, the present results have shown that because of exchanges, isotopes of hydrogen cannot be used in tracer studies on Friedel–Crafts alkylations with a high concentration of $AlCl_3$ as catalyst and with an excess of the arene being alkylated as solvent. Although it may be possible to decrease the extent of such exchanges by the use of an inert solvent, a weaker acid catalyst and a lower catalyst concentration, the present work has demonstrated that under the conditions usually employed, extensive and dynamic exchanges among both aromatic and side-chain H atoms do take place during a Friedel–Crafts reaction, even though the occurrence of such dynamic processes may not be apparent when the H atoms are not labeled.

Experimental Section

2-Phenyl[1-^{13}C]ethyl chloride (1-*1*-^{13}C) was prepared in the same way as previously described for the preparation of 1-*1*-^{14}C,[4] which involves reaction of benzylmagnesium chloride with [^{13}C]CO_2 to give phenyl[1-^{13}C]acetic acid, reduction with $LiAlH_4$ to 2-phenyl[1-^{13}C]ethanol, and then reaction with $SOCl_2$ in pyridine to give the desired 1-*1*-^{13}C. 2-[$^2H_5$]Phenyl[1-^{13}C]ethyl chloride (1-*1*-^{13}C-*2-Ph*-d_5) was obtained from a series of reactions starting with [$^2H_5$]bromobenzene via a Grignard reaction to give benzoic acid followed by $LiAlH_4$ reduction to benzyl alcohol and treatment with $SOCl_2$ to give the D-labeled benzyl chloride which was then converted to 1-*1*-^{13}C-*2-Ph*-d_5 as in the preparation of 1-*1*-^{13}C.

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Friedel-Crafts Reactions. A mixture of 1.0 g (6.8 mmol) of 1-*1*-^{13}*C*-*2*-*Ph*-d_5 and 1.5 g (11 mmol) of $AlCl_3$ in 5.0 mL of benzene or a mixture of 1.0 g (7.0 mmol) of 1-*1*-^{13}*C* and 1.5 g (11 mmol) of $AlCl_3$ in 5.0 mL of [$^2H_6$]benzene was heated under relux for 1 h. These conditions were chosen after preliminary trials which showed that longer reaction times at reflux temperature did not significantly improve the yields while reactions at room temperature failed to give appreciable yields of the product. The reaction mixture was worked up as previously described[1a] to give about 500 mg (about 40%) of 1,2-diphenylethane (**2**) which, after crystallization from 95% ethanol, melted at 52 °C (lit.[5] mp 52 °C). The mass spectra of samples of **2** were obtained with a Finnigan Model 3000 GC-MS instrument. Oxidation of **2** from the reaction of 1-*1*-^{13}*C*-*2*-*Ph*-d_5 with benzene in alkaline $KMnO_4$[1a] gave benzoic acid whose mass spectrum was also recorded.

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Registry No. 1-*1*-^{13}*C*, 35462-97-6; 1-*1*-^{13}*C*-*2*-*Ph*-d_5, 94371-69-4; **2**, 103-29-7; **2**-d_1, 94371-77-4; **2**-d_2, 94371-78-5; **2**-d_3, 94371-79-6; **2**-d_4, 94371-80-9; **2**-d_5, 94404-10-1; **2**-d_6, 94371-81-0; **2**-d_7, 94371-82-1; **2**-d_8, 94371-83-2; **2**-d_9, 94371-84-3; **2**-d_{10}, 94371-85-4; **2**-d_{11}, 94371-86-5; **2**-d_{12}, 94371-87-6; **2**-d_{13}, 94371-88-7; **2**-d_{14}, 94371-89-8; **2**-^{13}*C*, 61829-72-9; **2**-^{13}*C*-d_1, 94371-91-2; **2**-^{13}*C*-d_2, 94371-92-3; **2**-^{13}*C*-d_3, 94371-93-4; **2**-^{13}*C*-d_4, 94371-94-5; **2**-^{13}*C*-d_5, 94371-95-6; **2**-^{13}*C*-d_6, 94371-96-7; **2**-^{13}C-d_7, 94371-97-8; **2**-^{13}*C*-d_8, 94371-98-9; **2**-^{13}*C*-d_9, 94371-99-0; **2**-^{13}*C*-d_{10}, 94404-11-2; **2**-^{13}*C*-d_{11}, 94372-00-6; **2**-^{13}*C*-d_{12}, 94372-01-7; **2**-^{13}*C*-d_{13}, 94372-02-8; **2**-^{13}*C*-d_{14}, 94371-90-1; **3**, 65-85-0; **3**-d_1, 94371-70-7; **3**-d_2, 94371-71-8; **3**-d_3, 94371-72-9; **3**-d_4, 94371-73-0; **3**-^{13}*C*, 3880-99-7; **3**-^{13}*C*-d_1, 94371-74-1; **3**-^{13}*C*-d_2, 94371-75-2; **3**-^{13}*C*-d_3, 94371-76-3; H_2, 1333-74-0; $AlCl_3$, 7446-70-0; [^{13}C]CO_2, 1111-72-4; benzene, 71-43-2; [$^2H_6$]benzene, 1076-43-3; benzylmagnesium chloride, 6921-34-2; phenyl[1-^{13}C]acetic acid, 1563-79-7; 2-phenyl[1-^{13}C]ethanol, 35462-98-7; [$^2H_5$]bromobenzene, 4165-57-5; benzyl chloride, 100-44-7; benzyl alcohol, 100-51-6.

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The Stereospecific Total Synthesis of (±)-*cis*-Chrysanthemic Acid via the Alicyclic Claisen Rearrangement

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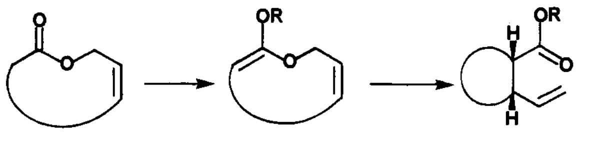
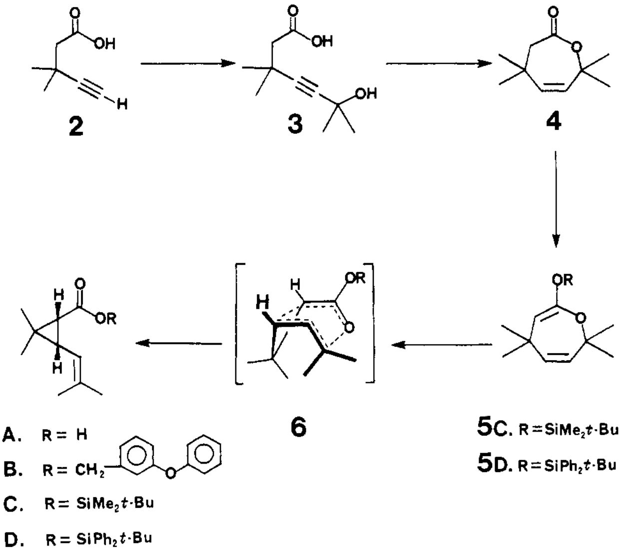
Pyrethroids are a class of powerful insecticides structurally related to the naturally occurring chrysanthemates.[1] The high insecticidal activity of the pyrethroids coupled with their low mammalian toxicity[2] has stimulated considerable synthetic activity in this area. Most of this effort has been directed toward the pyrethrins and cinerins, which are esters of *trans*-chrysanthemic acid or *trans*-pyrethric acid,[1] respectively. It has been discovered[3] that certain esters of *cis*-chrysanthemic acid possess superior activity relative to the *trans*-chrysanthemates, e.g., **1b**. Nevertheless, relatively few stereospecific total syntheses of the unnatural *cis*-chrysanthemic acid (**1a**) have been published.[4-6] Obviously, the major obstacle inherent in this synthetic problem is the cis relationship of the carboxy and alkenyl substituents on the cyclopropane ring.

Scheme I



Scheme II



We have recently reported a general, stereospecific synthesis of *cis*-2-alkenylcycloalkanecarboxylic acids via Claisen rearrangement mediated ring contraction of macrocyclic ketene acetals (Scheme I).[7] We now report the application of this methodology in a short, stereospecific synthesis of *cis*-chrysanthemic acid (**1a**).

The dianion of the readily available 3,3-dimethyl-4-pentynoic acid[8] (1 equiv of **2**, 2.1 equiv of *n*-BuLi, THF, -41 °C) was treated sequentially with lithium bromide[9] (0.5 equiv, THF, -41 °C) and dry acetone (1.1 equiv, -41 → 25 °C) to give the crystalline hydroxy acid **3** (mp 78-79 °C) in 65% yield (Scheme II). Catalytic semihydrogenation[10] of **3** ($Pd/BaSO_4$, quinoline, MeOH) gave a hydroxy acid which spontaneously lactonized to afford the desired Claisen rearrangement precursor, lactone **4** (mp

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