Acknowledgment. The authors gratefully acknowledge the financial support of this work by the National Institute of Neurological and Communicative Disorders and Stroke (Research Grant NS 120007) and the NSF for providing funds for a diffractometer facility (joint with Boston University).

Registry No.—**4b**, 66120-45-4; **4b**, HCl, 66120-46-5; **4** picrate, 66120-56-7; **5** isomer 1, 66120-47-6; **5** isomer 2, 66120-48-7; **5** isomer 1 HCl, 66120-49-8; **5** isomer 2 HCl, 66120-50-1; **6**, 66120-51-2; **8**, 66120-52-3; **9**, 66120-53-4; **9** HCl, 66120-54-5; **11**, 66120-55-6; 2,6-lutidine, 108-48-5; acetaldehyde, 75-07-0; glutaraldehyde, 111-30-8.

Supplementary Material Available: A table of final positional and thermal parameters (3 pages). Ordering information is given on any current masthead page.

References and Notes

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A Simple Carbon-13 Nuclear Magnetic Resonance Spectroscopic Method for Distinguishing between Open-Chain and Pseudoacid Chlorides

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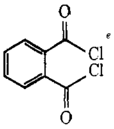
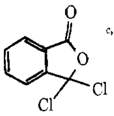
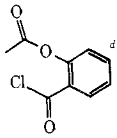
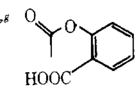
The structures of acid chlorides containing a carbonyl group at the γ position have been the subject of many reports. The possibility of the formation of cyclic forms (called pseudochlorides) of such molecules has been raised and substantiated in some cases. In many more instances, however, these structures have been postulated where evidence is weak or inconclusive. We wish to recommend a simple method that clearly distinguishes between pseudochloride and open-chain forms based on their ^{13}C magnetic resonance spectra.

The γ-diacid dichlorides are the most widely studied potential pseudochlorides. Phthaloyl chloride, for instance, has been isolated in two forms, and the higher melting isomer assigned the pseudochloride structure on the basis of dipole moment,[1] parachor,[2] and chemical reactivity.[3]

The γ-keto acid chlorides have been assigned the cyclic pseudochloride structure by chemical evidence,[4,5] infrared,[6] and ^1H NMR[7] spectroscopy.

The γ-ester acid chlorides are the group for which the evidence for the pseudochloride structure is least convincing. o-Acetoxybenzoyl chloride, for instance, has been found to exist in the open form by one set of chemical reactivity criteria[8] and to have a pseudochloride structure by another.[9] Infrared spectroscopy, in general, has given inconclusive results because of overlapping signals.[8] ^1H NMR spectroscopy has been employed to assign the open-chain structure to γ-carbomethoxypropionyl chloride on the basis of its methoxy proton signal at δ 3.66, compared to δ 3.29 for protons of this type in levulinic acid pseudomethyl ester, although the expected chemical shifts in the two pseudochlorides are not strictly comparable.[7]

Table I. ^{13}C Chemical Shifts of Aromatic Acid Chlorides

	Chemical shifts,[b] δ			
Carbon[a]	 [e]	 [c,f]	 [d,g]	 [h]
C-1′	167.3	169.1	164.5	170.0
C-2′	167.3	104.6		
Acetate C═O			168.9	169.7
Acetate CH_3			20.7	21.0
C-1	134.3	136.0	124.3	122.2
C-2	134.3	150.6	150.5	151.3
C-3	130.1	122.8	124.3	122.3
C-4	133.4	136.3	136.1	134.8
C-5	133.4	125.6	126.4	126.1
C-6	130.1	132.0	134.2	132.5

[a] Carbons are numbered as follows: C-1 is in the aromatic ring σ bonded to a carbonyl carbon (which is C-1′); C-2 is in the aromatic ring and bears the ortho substituent (C-2′); C-3 to C-6 then follow in sequence. [b] Assignments within a column that differ by less than 1 ppm should be regarded as tentative. [c] For preparation see ref 16. [d] For preparation see ref 14. [e] Registry no. 88-95-9. [f] Registry no. 601-70-7. [g] Registry no. 5538-51-2. [h] Registry no. 50-78-2.

Since molecules capable of existing as pseudochlorides were involved in synthetic work currently of interest in this laboratory, and because of the conflicting evidence available on the topic, the ^{13}C spectra of representative acid chlorides from each of the three groups were investigated. It was expected that π bonding and the magnetic anisotropy of the carbonyl group in the open-chain form would result in a large downfield chemical shift of this carbon signal in the ^{13}C spectra; such a large shift was not anticipated for the quaternary carbon in the pseudochloride structure.

Inspection of the first two entries of Table I substantiates this prediction. The lower melting phthaloyl chloride (entry 1) has carbonyl carbon absorptions at δ 167.3, reflecting its open-chain structure; the higher melting isomer (entry 2) has absorptions at δ 169.1 and 104.6, due to the carbonyl and quaternary carbons, respectively, in the cyclic pseudochloride structure. Moreover, the symmetry of the open-chain structure is revealed by having only three absorptions for the ring carbons; the nonsymmetrical pseudochloride has six additional peaks.

Clear evidence for the pseudochloride nature of levulinic acid chloride (entry 1, Table II) is seen in the ^{13}C spectrum, where only one carbonyl resonance is seen at δ 174.4. The resonance assigned to the quaternary carbon of the pseudochloride structure is again seen at δ 104.6, further substantiating the prediction made above.

Succinyl chloride (entry 2, Table II) is found to exist in the open-chain form, both on symmetry grounds (since only two resonances are seen in its ^{13}C spectrum) and by the chemical shift argument (the carbonyl resonance appears only at δ

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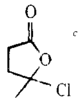
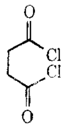
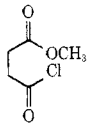
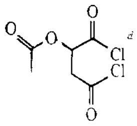
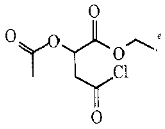
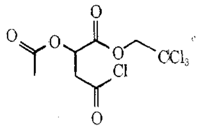
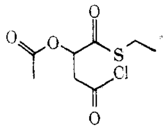
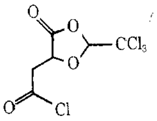
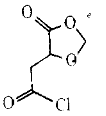
Table II. ^{13}C Chemical Shifts for Aliphatic Acid Chlorides

Structure[a]	Registry no.	Chemical shifts,[b] δ C-1	C-2	C-3	C-4	Acetate	Other
 [c]	40125-55-1	174.4	39.7	28.1	104.6		31.0 (CH_3)
	543-20-4	172.3	41.6	41.6	172.3		
	1490-25-1	171.2	29.1	41.7	172.8		51.9 (Me ester)
 [d]	65995-77-9	169.5	73.6	46.7	169.3	169.9 20.0	
 [e]	65995-82-6	167.5	67.4	47.5	169.5	169.9 20.1	62.2 13.8
 [e]	65995-78-0	166.2	66.9	47.1	169.4	169.6 20.1	74.5 105.3
 [e]	65995-79-1	106.9	73.3	48.0	169.2	169.6 20.4	23.2 14.2
 [f]	65995-80-4	170.8	70.8	47.3	169.0		122.1 105.0
 [e]	65995-81-5	171.0	69.1	46.9	169.1		95.2

[a] Carbons are numbered as follows: C-1 of levulinate is the carbonyl carbon; C-2 of malate derivatives is σ bonded to an oxygen; C-1 of γ-carbomethoxypropionyl chloride is the ester carbonyl. [b] Assignments for a given compound that differ by less than 1 ppm should be regarded as tentative. [c] For preparation see ref 17. [d] For preparation see ref 18. [e] For preparation see ref 19. [f] For preparation see ref 20.

172.3, and there is no resonance between δ 80 and 120). This substantiates previous work,[1,2,4,10,11,12] in which only the open-chain form has been found.[13,14]

According to the ^{13}C spectrum, o-acetoxybenzoyl chloride (entry 3, Table I) exists as an open-chain structure, since two carbonyl resonances are seen at δ 164.5 and 168.9, and no signal is observed between δ 80 and 120. The signal at δ 164.5 is assigned to the acid chloride carbonyl carbon by comparison to the parent acid (entry 4, Table I). The chemical shift change of 6 ppm upfield from acid to acid chloride is similar to that found in other cases.[15]

The other entries in Table II are ester acid chlorides, all capable of existing in pseudochloride form. The ^{13}C NMR data show that each has an absorption in the carbonyl region (δ 169–170) for the acid chloride and none in the δ 80–100 region; thus all exist as open-chain structures.

The ^{13}C NMR technique thus provides a method for distinguishing between pseudo- and open-chain chlorides, which is capable of observing the presence of even a small fraction of the tautomeric structure.

Experimental Section

Samples for analysis were prepared in $CDCl_3$ at 5–10% (w/v) concentrations with Me_4Si (0.1%) as internal standard. Sample temperature during irradiation was maintained at 300 K. ^{13}C NMR spectra were recorded on a Bruker HX-90E spectrometer operating at 22.63 MHz in the pulsed Fourier transform mode with a deuterium lock. Free induction decay data were accumulated using 8192 data points for a sweep width of 5000 Hz and processed with a Nicolet 1089 computer. Data were acquired both with and especially without simultaneous broad band irradiation of protons at 90 MHz in order to intensify the carbonyl and quaternary carbon signals, relative to other signals. Carbon nuclei were pulsed with a 90° tilt angle using a 40-μs pulse; the interval between pulses was often 60 s or more. Accumulations were continued until the signal/noise ratio on the least intense peak was at least 20:1 using spectral smoothing amounting to line broadening of 1 Hz. Thus it would be expected that signals from tautomeric structures comprising 5% or more of the sample would have been observed. Chemical shift assignments were made by single-frequency off-resonance decoupling experiments, single-frequency proton irradiation, and reference to other compounds.[15] These methods allowed unequivocal assignments for all but aromatic or carbonyl carbons. Such resonances were assigned by comparison within the series, so that uncertainty exists only for those signals differing by less than one part per million.

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Synthesis and Thermal Rearrangements of Methylenecyclobutanes

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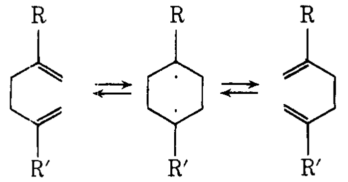
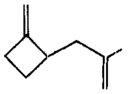
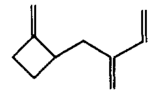
The Cope and Claisen rearrangements play a prominent role in contemporary synthetic organic chemistry; an understanding of the influence of substituents on the rate and mechanism of these reactions is of considerable importance.[1,2] Relatively few quantitative studies of this type, however, are available.[3] The influence of substituents at the 2 and 5 positions of 1,5-hexadiene is particularly important in the longstanding question regarding the possible intervention of 1,4-diradical intermediates in [3,3] sigmatropic rearrangements (eq 1).[4] We report here the synthesis and thermal rearrangements of methylenecyclobutanes 1 and 2; a kinetic analysis of their thermal chemistry permits us to document the influence of a vinyl substituent in the Cope rearrangement.



(1)

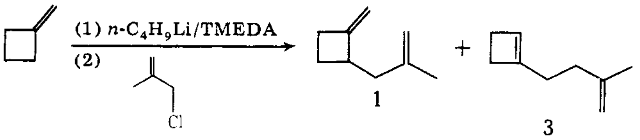


1



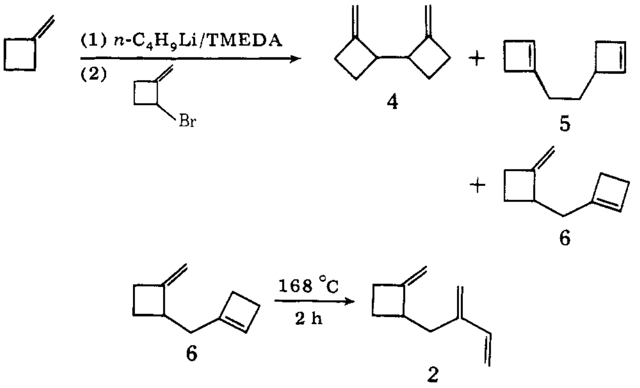
2

2-(2-Methyl-2-propenyl)methylenecyclobutane (1) was prepared by the reaction of 1-cyclobutenylmethyllithium with methallyl chloride.[5] The products (90%) consist of a mixture of isomers (1/3) in a ratio of 85:15. Pure 1 was isolated by preparative VPC. Compound 2 was obtained by the procedure outlined in Scheme I. Condensation of 2-bromomethylenecyclobutane with 1-cyclobutenylmethyllithium results in the formation of three isomeric $C_{10}H_{14}$ hydrocarbons, 4–6.[6] The unsymmetrical coupling product 2-(1-cyclobutenylmethyl)methylenecyclobutane (6), when heated for 2 h at 168 °C, yields triene 2 and two additional isomeric olefins (vide infra).



Thermolysis of methylenecyclobutanes 1 and 2 initiates the sequence of rearrangements shown in Scheme II. Both Cope rearrangement products (3 and 8) react further via electrocyclic ring opening to produce polyenes 7 and 9. During the course of our investigations it was noted that the rearrangement of 2 occurs under significantly milder conditions than that of 1. This observation was quantified in the following manner. The rate of Cope rearrangement of 1 (k_1) was determined by monitoring its rate of disappearance over a range of temperatures (gas phase, sealed tubes) and extrapolating, $k_1(170.6\ °C) = 5.47 \times 10^{-7} s^{-1}$. The rate of electrocyclic ring opening ($3 \rightarrow 7$) was also measured, $k_2(170.6\ °C) = 5.19 \times 10^{-4} s^{-1}$.[7] The rate of Cope rearrangement of 2, k_3, was calculated as follows. Disappearance of 2 at 170.6 °C was found to be $k_{obsd} = 3.75 \times 10^{-5} s^{-1}$. The ratio of k_4/k_{-3} was obtained from the rate of appearance of 9 and 2 during the initial stages of the reaction of 8, $k_4/k_{-3} = 2.97$. A steady state approximation was then used to calculate k_3. The validity of this approximation was confirmed by computer simulation of concentration vs. time plots (assuming $k_2 = k_4$) using the MSIM4 program.[8] The best value for the rate of Cope rearrangement of 2 was found, $k_3(170.6\ °C) = 5.01 \times 10^{-5} s^{-1}$. Using this number to calculate the relative rate of Cope rearrangement, $2/1 = k_3/k_1 = 91$ (170.6 °C).

Scheme I



Scheme II