Stable Carbocations. CLXV.[1] Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of Alkenoyl Cations. The Importance of Delocalized "Ketene-like" Carbenium Ion Resonance Forms

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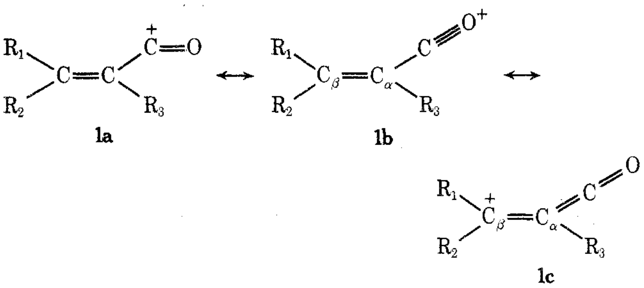
The proton-coupled carbon-13 nmr spectra of a series of alkenoyl cations in SO_2-SbF_5 solution have been studied by the Fourier transform method. Comparison of the data with chemical shifts and ^{13}C-H coupling constants in the acid chloride precursors and with ketene, a suitable model compound, indicate that there is substantial contribution to the structure of alkenoyl cations from delocalized "ketene-like" resonance forms.

The preparation and proton nmr spectra of a series of alkenoyl cations 1 have been reported by Olah and Comisarow.[4] Since carbon-13 nmr spectral studies[5] were able to show more adequately than pmr spectral studies that there are significant contributions to the structure of aroyl cations from delocalized "ketene-like" resonance forms, we decided to examine further the structure of the related alkenoyl cations by cmr spectroscopy.

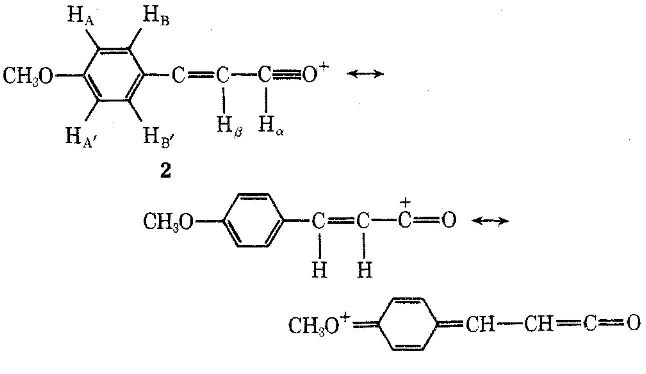

1a 1b 1c

Results and Discussion

Preparation of Alkenoyl Ions and Their Pmr Spectra. The α,β-unsaturated alkenoyl cations in Table II whose syntheses have not been reported[4] were prepared by the same or slightly modified general method (see Experimental Section). Pmr spectral parameters for previously prepared ions in Table II have been reported.[4]

The pmr spectrum of the 3,3-diphenylpropenoyl cation in SbF_5-SO_2 at $-70°$ consists of signals at δ 6.88 (s, 1, C=CH) and 7.6-8.4 (m, 10, aromatic). On warming the solution to $-40°$, another set of absorptions appeared at δ 7.32 (s) and 8.7-9.3 (m), indicating that decomposition of the ion was occurring. The decomposition product is irreversibly formed and as yet has not been identified.

A solution of the 3-(*p*-anisyl)propenoyl cation (*E*)[6] 2 in SO_2 at $-60°$ gives a pmr spectrum with signals at δ 4.73 (s, 3, OCH_3), 7.08 (d, 1, J = 17.0 Hz, H_α), 7.8 (d, 2, $J \cong 8$ Hz, H_A and $H_{A'}$), 8.34 (d, 2, $J \cong 8$ Hz, H_B and $H_{B'}$), and 9.4 (d, 1, J = 17.0 Hz, H_β). The ion decomposes slowly at this temperature and a satisfactory cmr spectrum could not be obtained.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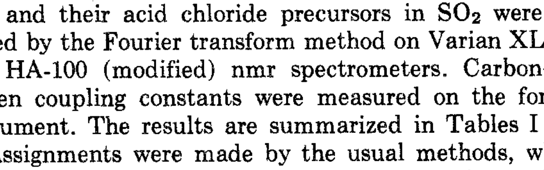
The carbocation formed when fumaroyl chloride was treated with an excess of SbF_5-SO_2 shows a pmr spectrum with absorptions at δ 8.55 (d, 1, J = 17.5 ± 0.1 Hz, H_A), 9.28 (d, 0.5, J = 17.5 ± 0.1 Hz, H_B or H_C), and 9.33 (d, 0.5, J = 17.5 ± 0.1 Hz, H_C or H_B). The observed pmr and subsequently discussed cmr (Table II) spectral parameters were accounted for by the monocation monodonor-acceptor complex (3), in which SbF_5 is complexed to the carbonyl oxygen in cis and trans configurations.[7] The nonequivalence of H_B (H_C) arises from the slow (on the nmr "time scale") equilibrium 3a ⇌ 3b. The equilibrium is still slow at $-20°$, since there is no change in the pmr spectrum at this temperature.


3a 3b

Cmr Spectroscopic Studies. The proton-decoupled carbon-13 nmr spectra of solutions of alkenoyl cations in SbF_5-SO_2 and their acid chloride precursors in SO_2 were obtained by the Fourier transform method on Varian XL-100 and HA-100 (modified) nmr spectrometers. Carbon-hydrogen coupling constants were measured on the former instrument. The results are summarized in Tables I and II. Assignments were made by the usual methods, which included "off-resonance" proton decoupling, the applications of previously observed substituent effects, as well as symmetry and relative intensity considerations.

We are changing with this publication to give cmr shifts in reference to tetramethylsilane, instead of carbon disulfide used in our previous work. This more consistent and convenient reference is gaining general acceptance. [The conversion factor for CS_2 is 193.8 (capillary), 192.8 (external)].

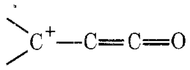
A. Cmr Spectra of Precursor Alkenoyl Halides. The cmr spectra of most alkenoyl chloride precursors are as expected. The ^{13}C carbonyl shifts of the acyl chlorides appear 4-8 ppm shielded from the corresponding resonances in carboxylic acids.[8] A similar order is also observed for alkenoyl chlorides and their corresponding carboxylic acids;[9a] only the difference is smaller (1-4 ppm).

The deshielding (Table I) of the β carbon, that occurs on replacement of a hydrogen in the parent olefin ($R_1R_2C{=}CHR_3$) with a COCl group, may be rationalized in terms of a contribution to the structure of alkenoyl chlorides from the resonance form $R_1R_2{}^+CCR_3{=}C(Cl)O^-$ All α-carbon shieldings are also deshielded by the COCl group with respect to the parent olefin,[9b] but to a lesser extent than the β carbon.

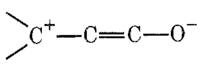
The effect of the COCl group on a cis methyl carbon shielding is evident from the 5.7-ppm shift difference in the two methyl carbon shieldings of 3,3-dimethylpropenoyl chloride. Similarly, a difference of 2.0 ppm is found in the two ipso carbon shieldings of 3,3-diphenylpropenoyl chloride.

Carbon-hydrogen coupling constants in alkenoyl chlorides are also shown in Table I. $J_{C\beta-H}$ in propenoyl chloride is given as a single value, although in most vinyl derivatives[9c] $J_{C\alpha-H(cis)}$ and $J_{C\beta-H(trans)}$ have been shown to be slightly different. The effect of the polar COCl substituent on $J_{C\alpha-H}$ is seen by the larger values of $J_{C\alpha-H}$ in propenoyl, butenoyl, and 3,3-dimethylpropenoyl chlorides than in the appropriate parent olefins.

B. Cmr Spectra of Alkenoyl Cations. Carbon-13 nmr spectral parameters of alkenoyl cations studies are summarized in Table II. The changes of cmr parameters occurring in acid chlorides upon ionization with SbF$_5$ are shown in Table III. In the case of propenoyl chloride there is a deshielding of 39.8 ppm at C$_\beta$, which we interpreted to be a result of a larger contribution of resonance form **4a** to the structure of the alkenoyl cation than that of resonance form **4b** to the structure of the alkenoyl chloride precursor. Shift differences of this magnitude between alkenoyl cation and precursor could hardly arise from just neighboring-group effects (*e.g.*, solvent and antisotropy effects), nor could differences in the local diamagnetic term σ_d be invoked,[10] since the same substituents are attached to C$_\beta$ in ion and precursor. The C$_\beta$ shift in the propenoyl cation is the most deshielded (by about 40 ppm) β-carbon shift observed in vinyl derivatives.[9c]



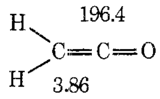
4a



4b

In keeping with the above structural views, it was found that attachment of a stabilizing alkyl, cycloalkyl, or aryl group to C$_\beta$ gave an even larger deshielding at C$_\beta$ in the resulting ion. The deshielded para carbon resonance in the 3-phenylpropenoyl cation is additional evidence for delocalized "ketene-like" resonance forms. Attachment of a methyl group at C$_\alpha$ has very little effect on β-carbon shift, but an electron-withdrawing group such as COCl → SbF$_5$ at C$_\beta$ results in a much smaller deshielding (compared with the propenoyl cation) upon ionization of the acid chloride (Table III).

On ionization of propenoyl chloride with SbF$_5$, a large shielding effect of 38.7 ppm at C$_\alpha$ is observed. Apart from vinyl iodide,[9d] where "heavy atom" effects operate, this is the most shielded shift yet observed for C$_\alpha$ in a vinyl derivative. As for neutral vinyl compounds, the C$_\alpha$ shielding is more difficult to rationalize than the C$_\beta$ shielding. However, the shielded (compared with a normal alkene carbon) terminal carbon shift (^{13}C δ 3.86) in the model compound, ketene, suggests that the large shielding in the α-carbon shift which occurs in the alkenoyl chlorides upon ionization arises from a significant contribution from the "ketene-like" resonance form **1b** in the ionized species.



$J_{C-H} = 175.9 \pm 0.4$ Hz

Consistent with this viewpoint, ions with a substituent at C$_\beta$, which is capable of stabilizing an adjacent carbenium ion center, have the most shielded C$_\alpha$ shifts (Table III).

This observation is consistent with the relatively deshielded (compared with the carbonyl shift of acyl cations) central carbon shift in ketene. The carbonyl shifts in alkenoyl cations are most deshielded in those ions which have the most deshielded C$_\beta$ shifts and the most shielded C$_\alpha$ shifts, *i.e.*, those ions which have the largest contribution to their structure from the delocalized "ketene-like" resonance form.

To determine the extent of the contribution from "ketene-like" resonance forms we have observed the pmr spectrum of 3-methyl-2-propenoyl cation over a range of temperatures. At 80°, where decomposition of the ion began to occur, there was no change in the position of the two nonequivalent methyl signals, indicating that at this temperature rotation about the C$_\alpha$-C$_\beta$ bond was still slow on the nmr "time scale." Therefore, although there is a substantial contribution from resonance form **1c**, it appears that forms **1a** and **1b** are still major contributors.

The value of the C$_\alpha$-H coupling constant in the propenoyl cation is 28 Hz larger than the corresponding value in the acid chloride precursor. This most likely is a result of the greater electronegativity of the C≡O$^+$ group compared with the COCl group. The same trend is also apparent for all the alkenoyl cations in Table II. $J_{C\beta-H}$ in these ions is also larger than in the precursors, but to a lesser extent.

In the alkenoyl cations in Table II, as the contribution of the "ketene-like" resonance form increases there is a corresponding decrease in $J_{C\alpha-H}$ until in the 3,3-diphenylpropenoyl cation, $J_{C\alpha-H}$ is only slightly larger than the C-H coupling constant of ketene (175.9 Hz). This trend is additional evidence for the structural considerations outlined above for alkenoyl cations.

Experimental Section

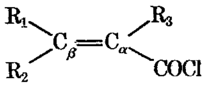
Propenoyl, isopropenoyl, (*E*)-2-butenoyl, (*E*)-2-methyl-2-butenoyl, 3,3-dimethylpropenoyl,[12] fumaroyl, 3-phenylpropenoyl, and 3-(*p*-anisyl)propenoyl[13] chlorides were either commercially available or were prepared from the appropriate carboxylic acid and thionyl chloride by usual procedures. Attempts to prepare (*Z*)-2-butenoyl chloride from the unstable 2-butenoic acid[14] and thionyl chloride gave only *E*-2-butenoyl chloride. 3,3-Diphenylpropenoyl chloride was prepared from the reaction of 1,1-diphenylethene with oxalyl chloride,[15] pmr (CCl$_4$) δ 6.52 (s, 1, C=CH), 6.8-7.7 (m, 10, C$_6$H$_5$). Ketene prepared by the described procedure[16] had a pmr spectrum consistent with the reported data.[17]

(*E*)-3-Cyclopropyl-2-butenoic Acid. A 3.6-g (0.028 mol) portion of ethyl (*E*)-3-cyclopropyl-2-butenoate[18] was heated under reflux for 1 hr in a solution of 3.6 g of sodium hydroxide in ethanol (40 ml) and water (3 ml). The reaction mixture was cooled and concentrated, and the residue was dissolved in a minimum amount of water. The aqueous solution was washed with ether (2 × 20 ml), acidified with 10% hydrochloric acid, and extracted with ether (2 × 100 ml). The combined ether extracts were dried (MgSO$_4$) and concentrated to give the crude acid. Recrystallization from petroleum ether (bp 60-80°) afforded 2.7 g (90%) of (*E*)-3-cyclopropyl-2-butenoic acid: mp 101-102° (lit.[19] mp 99-100°); nmr (CCl$_4$) δ 0.67-0.89 (m, 4, CH$_2$), 1.28-1.80 (m, 1, CH), 2.0 (s, 3, CH$_3$), 5.68 (s, 1, C=CH), 12.12 (s, 1, COOH).

Reaction of (*E*)-3-Cyclopropyl-2-butenoic Acid with Thionyl Chloride. A 1-g portion of (*E*)-3-cyclopropyl-2-butenoic acid was stirred at room temperature with 1 ml of thionyl chloride and 10 ml of carbon tetrachloride. The solvent and excess thionyl chloride were removed with a rotatory evaporator, using a water bath at room temperature. The nmr spectrum of the crude product indicated it to be predominantly 3-cyclopropyl-2-butenoyl chloride and an impurity which could not be separated by fractional distillation. This as yet unknown by-product was also present when the reaction was repeated at different temperatures, or in the absence of solvent: ir (film) 1755 (C=O) and 1578 cm^{-1}; nmr (CCl$_4$) δ 0.4-1.05 (CH$_2$), 1.6-2.2 (CH), 1.65 (CH$_3$), 1.9 (CH$_3$), 6.02 (C=CH).

3,3-Dicyclopropyl-2-propenoic Acid. A 1.8-g (0.01 mol) portion of ethyl 3,3-dicyclopropyl-2-propenoate[18,20] was heated under reflux for 1 hr in a solution of 1.5 g of sodium hydroxide in ethanol (20 ml) and water (1 ml). The product was isolated in the usual method and recrystallized from petroleum ether to give 1.05 g (82%) of 3,3-dicyclopropyl-2-propenoic acid: mp 136-137°; ir (Nujol) 3200-2600 (OH), 1695 (C=O), 1590 cm^{-1} (C=C); nmr (CCl$_4$) δ 0.47-1.15 (m, 10, cyclopropyl), 5.4 (s, 1, C=CH), 12.1 (s,

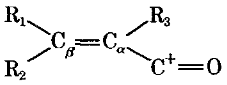
Table I
Carbon-13 Shielding[a] and Carbon–Hydrogen Coupling Constants[b] of α,β-Alkenoyl Chlorides[c]



Registry no.	Substituent			Chemical shift				Coupling constants		
	R_1	R_2	R_3	Cα	Cβ	CO	Others	$J_{C\alpha-H}$	$J_{C\beta-H}$	Others
814-68-6	H	H	H	131.4	137.3	165.6		173.2 ± 0.5	164.2	
625-34-4	CH_3	H	H	126.1	155.2	165.8	18.4 (CH_3)	171.4	163 ± 1	128.2 (J_{CH_3})
3350-78-5	CH_3	CH_3	H	121.5	163.2	166.9	27.4 (CH_3) 21.7 (CH_3)	172.1		128.3 (J_{CH_3}) 130.8 (J_{CH_3})
920-46-7	H	H	CH_3	140.5	135.4	169.0	18.0 (CH_3)		161.5	127.1 (J_{CH_3})
35660-94-7	H	CH_3	CH_3	132.7	149.6	169.0	15.6 (CH_3) 13.1 (CH_3)		158 ± 2	127.5 (J_{CH_3}) 128.8 (J_{CH_3})
4456-79-5	C_6H_5	C_6H_5	H	121.5	162.3	164.2	137.6, 139.6 (C_i) 132.0, 130.1 (C_p) 129.8 (C_m) 129.4, 128.9 (C_o)	*f*	*f*	*f*
645-45-4	C_6H_5	H	H[d]	116.9	143.2	167.2	132.5 (C_i) 128.5 (C_p) 127.0 126.3	160.3	156.5	161.5 (J_{C_p-H}) 162.5 160.4
42996-84-9	*p*-$CH_3OC_6H_4$	H	H[e]	119.0	152.1	167.2	162.6 (C_i) 115.1 132.0 55.0 (CH_3O)	165.6	156.2	162.7 164.9 147.1 (J_{OCH_3})
50921-72-7	c-$C_3H_5(CH_3)$	CH_3(*c*-C_3H_5)		121.4	175.1	163.3	9.3, 10.1 (CH_2) 21.5, 26.2			
627-63-4	COCl	H	H	140.3	140.3	166.2		176.1	176.1	

[a] Parts per million from external capillary of tetramethylsilane. [b] Hertz. Precision is ±0.3 Hz. [c] In SO_2 at −40° unless otherwise indicated. [d] In $CDCl_3$. [e] In SO_2 at −25°. [f] Poor-quality proton-coupled spectrum.

Table II
Carbon-13 Shieldings and Carbon–Hydrogen Coupling Constants in Some α,β-Alkenoyl Cations[a]



Registry no.	Substituent			Chemical shift[b]				Coupling constants[c]		
	R_1	R_2	R_3	Cα	Cβ	CO	Others	$J_{C\alpha-H}$	$J_{C\beta-H}$	Others
35335-84-3	H	H	H	92.7 (30.1)[d]	177.1 (54.3)[d]	147.1		201.0	176.5	
50921-73-8	CH_3	H	H	84.3	202.6	151.5	26.7 (CH_3)	197.6	168.3	131.3 (J_{CH_3})

44391-34-6	CH_3	CH_3	H	79.0	223.0	154.2	30.0 (CH_3) 28.6 (CH_3)	192.6		130.8 (J_{CH_3}) 128.0 (J_{CH_3})
44158-09-0	H	H	CH_3	104.3	172.8	148.1	16.0		173.9 ± 0.8	132.7 (J_{CH_3})
44367-88-6	H	CH_3	CH_3	94.3	193.5	151.3	21.7 (CH_3) 10.5		165.2	132.3 (J_{CH_3}) 136.6 (J_{CH_3})
50921-56-7	C_6H_5	C_6H_5	H[e]	68.7	201.1	158.7	136.0, 135.7 (C_i) 134.7, 132.7 (C_o) 131.0, 130.5 (C_m) 140.2, 138.5 (C_p)	180 ± 5		[f]
35335-84-3	C_6H_5	H	H	69.4	183.3	157.0	131.6 (C_i) 133.9 (C_o) 130.0 (C_m) 142.1 (C_p)	191.3	166.0	165.6 (J_{C_p-H}) 168.5 (J_{C_m-H})
50921-70-5	c-C_3H_5	CH_3	H[g]	71.2	227.0	160.4	32.3 (CH) 25.2 (CH_2) 22.4 (CH_3)	185 ± 5		
50921-22-7	COCl– SbF_5	H	H	102.8	165.3 162.0	146.7 143.1	157.1 (COCl)– SbF_5	206.4	190 ± 1	

[a] In SO_2 at −40° unless otherwise indicated. [b] Parts per million from external capillary of 5% ^{13}C-enriched tetramethylsilane. In several cases where the HA-100 nmr spectrometer was used, shifts were measured from external capillary of 70% ^{13}C-enriched methyl iodide (lock signal) and converted using $\delta(CH_3I)$ −20.2. This conversion factor is temperature dependent, changing 0.029 ppm per centigrade degree. [c] Hertz. Precision in ±0.3 Hz. [d] Deshielding from ethane. [e] In SO_2 at 70°. [f] Aromatic signals too complicated in coupled spectrum. [g] In SO_2 at −80°.

Table III
Changes in Carbon-13 Shieldings and Carbon–Hydrogen Coupling Constants upon Formation of the Alkenoyl Cations from the α,β-Alkenoyl Chlorides

Substituent[a]			Chemical shift[b]				Coupling constants[c]	
R_1	R_2	R_3	Cα	Cβ	CO	Others	Cα	Cβ
H	H	H	−38.7	39.8	18.5		27.8	12.3
CH_3	H	H	−41.8	47.2	14.3	8.3 (CH_3)	26.3	5
CH_3	CH_3	H	−42.5	59.8	12.7	2.6 (CH_3) 6.9 (CH_3)	20.5	
H	H	CH_3	−36.2	37.4	21.6	2.0 (CH_3)		12.4
H	CH_3	CH_3	−38.4	43.9	17.7	6.1 (CH_3) 2.6 (CH_3)		4
C_6H_5	C_6H_5	H	−52.8	38.8	5.5			
C_6H_5	H	H	−47.5	40.1	10.2	−0.9 (C_i) 13.6 (C_p)	31.0	9.5
c-C_3H_5	CH_3	H	−50.2	52.1	2.9	15.9 (CH_2) 0.9 (CH_3)		
COCl	H	H	−37.5	25.0 21.7	19.5 23.1		30.3	14

[a] R_1, R_2, and R_3 refer to structures in Tables I and II. [b] Parts per million. Positive sign indicates deshielding in the alkenyl oxocarbenium ion. [c] Hertz. Positive sign indicates increased coupling constant in the alkenoyl cation.

1, COOH). *Anal.* Calcd for $C_9H_{12}O_2$: C, 71.01; H, 7.96. Found: C, 70.94; H, 7.96.

Attempts to prepare the acid chloride by the reaction of the acid with thionyl chloride under a variety of conditions were unsuccessful, and gave complex mixtures of unidentified products.

Preparation of Ions. Solutions of alkenoyl cations were prepared by adding the appropriate alkenoyl chloride, either directly or as a saturated SO_2 solution at −78°, to an excess of SbF_5 in SO_2 at −78°.

Proton Nuclear Magnetic Resonance Spectra. Pmr spectra were obtained using Varian Associates Model A56/60A and HA-100 spectrometers equipped with variable-temperature probes. External tetramethylsilane (capillary) was used as reference. Pmr spectra of ions reported previously were found identical with described spectra.[4]

Carbon-13 Nuclear Magnetic Resonance Spectra. A Varian Associates Model XL-100 spectrometer equipped with a broad-band proton decoupler and variable-temperature probe was used. The instrument operates at 25.2 MHz for ^{13}C, and is interfaced with a Varian 620-L computer. The combined system was operated in the pulse-Fourier transform mode, employing a Varian Fourier transform accessory. Typically 3000-5000 pulses, each of width 20-30 μsec, needed to be accumulated in order to give a satisfactory signal-to-noise ratio for all signals of interest. Field-frequency stabilization was maintained by locking on the ^{19}F signal of an external sample of fluorobenzene. Chemical shifts were measured from the ^{13}C signal of 5% ^{13}C-enriched tetramethylsilane in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube.

Some spectra were obtained using a Varian Associated Model HA-100 nmr spectrometer equipped with a Fourier transform accessory (V-4357 Pulsing and Control Unit), broad-band proton decoupler, and variable-temperature probe. The instrument, lock, and referencing systems have been described in more detail elsewhere.[21]

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No.—(*E*)-3-Cyclopropyl-2-butenoic acid, 50921-71-6; ethyl (*E*)-3-cyclopropyl-2-butenoate, 21014-28-8; 3,3-dicyclopropyl-2-propenoic acid, 37520-24-4; ethyl 3,3-dicyclopropyl-2-propenoate, 21046-02-6.

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Reactions of Sulfur Diimides with Phenyl- and Phenylchloroketenes

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The reactions of sulfur diimides **1a–d** with phenylketene (**2a**) below −50° gave 1-substituted 3,4-diphenylpyrroline-2,5-diones **6a–d** and 2-substituted 4,5-diphenyl 5-substituted carbamoyl-1,2-thiazolidin-3-ones **7a–d** as major products. Reduction of **7a** by Raney Ni afforded only *N,N'*-di-*tert*-butyl-2,3-diphenylbutane diamide (**11a**) in 85% yield, while **7b** and **7c** under the identical condition led to the corresponding amides, **11b** (70%) and **11c** (44%), and 1-substituted 3,4-diphenyl-4-carbamoylazetidin-2-ones, **12b** (12%) and **12c** (16%), respectively. Oxidation of **7a–d** by *m*-chloroperbenzoic acid gave 1,2-thiazolidin-3-one 1-oxides **13a–d** in good yields. The reactions of sulfur diimides **1b and 1c** with phenylchloroketene (**2b**) yielded similarly **6b and 6c** as the major product, but the reaction of **1d** afforded mainly 1,3,4-triphenyl-3,4-dichloropyrrolidine-2,5-dione (**16d**). The formation mechanism of the above products was discussed.

In previous work[1] we investigated the reactions of sulfur diimides with ketenes and found that the reaction products depend on substituents both on the starting sulfur diimides and ketenes, that is, (a) in the reaction with diphenylketene, diphenylsulfur diimide gave 1:2 and 1:1 cycloadducts at low and at high temperatures, respectively, and di-*tert*-butylsulfur diimide afforded two types of 1:1 cycloadducts; (b) in the reaction with alkylketenes, sulfur diimides afforded no cycloadduct but the unexpected thiobis(amine) derivatives, regardless of the substituents on the sulfur diimides. Further results on substituent effects in these reactions are reported in this paper.

Results and Discussion

Reaction of Sulfur Diimides with Phenylketene. The reactions of sulfur diimides **1a–d** with phenylketene (**2a**) (Scheme I), generated *in situ* from phenylacetyl chloride and triethylamine, unexpectedly gave 1-substituted 3,4-diphenlypyrroline-2,5-diones **6a–d** and 2-substituted 4,5-diphenyl 5-substituted carbamoyl-1,2-thiazolidin-3-ones **7a–d,** which arise from 1 mol of **1** and 2 mol of **2a,** along with small amounts of some by-products.

The reaction products were independent of the ratio of **1** to **2a** used in the reaction. The structure of **7** was established by a combination of spectral and chemical evi-