for the non-hydrogen atoms and isotropic temperatures factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are $R = 0.043$ and $R_w = 0.036$ for the 1201 observed reflections. The final differences map has no peaks greater than ± 0.2 e A^{-3}.

(*Z*)-*rac*-4-[2-(4,5-Dihydro-1*H*-imidazol-2-yl)-1-phenylcyclopropyl]phenol Hydrochloride (11). A suspension of 81 mg (0.22 mmol) of **9** and 43 mg of 10% palldium on carbon in 2 mL of ethanol, 0.3 mL of 3.9 M ethanolic hydrochloric acid, and 1.0 mL of cyclohexene was heated to reflux for 5 h. The residue obtained after filtration and evaporation was recrystallized from ethanol–ether to give 41 mg (59%) of **11**: mp 203–204 °C; ^{1}H NMR (Me_2SO-d_6) δ 1.79 (dd, 1 H, J = 6 Hz, 10 Hz), 2.37 (t, 1 H, J = 6 Hz) 2.71 (dd, 1 H, J = 6 Hz, 10 Hz), 3.45–3.75 (m, 4), 6.73 (d, 2 H, J = 9 Hz), 7.15 (d, 2 H, J = 9 Hz), 7.21–7.46 (m, 5), 9.55 (s, 1 H), 9.88 (s br, 2 H).

Anal. Calcd for $C_{18}H_{18}N_2O$·HCl: C, 68.67; H, 6.08; N, 8.90; Cl, 11.26. Found: C, 68.62; H, 6.03; N, 8.82; Cl, 11.49.

(*E*)-*rac*-4-[2-(4,5-Dihydro-1*H*-imidazol-2-yl)-1-phenylcyclopropyl]phenol Hydrochloride Ethanolate (12). A suspension of 0.60 g (1.63 mmol) of **10** and 0.20 g of 10% palladium on carbon in 15 mL of ethanol, 2 mL of 3.9 M ethanolic hydrochloric acid, and 7.5 mL of cyclohexene was heated to reflux for 3 h. The residue obtained after filtration and evaporation was crystallized from ethanol–ether to give 0.48 g (94%) of **12**: mp 130–134 °C; ^{1}H NMR (Me_2SO-d_6) δ 1.06 (t, 3 H, J = 7 Hz), 1.76 (dd, 1 H, J = 6 Hz, J = 9 Hz), 2.37 (t, 1 H, J = 6 Hz), 2.67 (dd, 1 H, J = 6 Hz, J = 9 Hz), 3.40–3.75 (m, 6 H), 6.68 (d, 2 H, J = 9 Hz), 7.24 (d, 2 H, J = 7 Hz), 7.34 (m, 5 H), 9.45 (s, 1 H), 9.87 (s br, 2 H); MS, m/e (relative intensity) 268 (38), 201 (100).

Anal. Calcd for $C_{18}H_{18}N_2O$·HCl·C_2H_5OH: C, 66.56; H, 6.98; N, 7.76; Cl, 9.83. Found: C, 66.57; H, 6.96; N, 7.76; Cl, 10.25.

5,5-Diphenyl-2-pyrrolidinone (16). A solution of phosphorus pentoxide in methanesulfonic acid was prepared by stirring a 1:10 (w/w) mixture of P_2O_5 and methanesulfonic acid at 100 °C under argon until the solution was homogeneous (45 min). To 260 g of this mixture was added 30 g (0.126 mol) of amide **15**, and the resulting mixture was stirred at 80–90 °C for 6 h. After cooling, the mixture was slowly poured into 600 mL of ice-cold water, and the resulting suspension was stirred at room temperature for 1 h. The crystals were filtered, washed with water, and dried overnight under suction in a Büchner funnel to give 30 g of crude lactam. This was recrystallized from 600 mL of 2:1 ethyl acetate–hexane to give 18.1 g (60%) of lactam **16**, mp 190–192 °C (lit.[6] mp 188–189 °C).

3,4-Dihydro-5-methoxy-2,2-diphenyl-2*H*-pyrrolium Tetrafluoroborate (17·HBF$_4$). A solution of 2.85 g (12 mmol) lactam **16** in 50 mL of methylene chloride was treated with 1.80 g (12.2 mmol) of trimethyloxonium tetrafluoroborate,[7] and the resulting suspension was stirred at room temperature under argon for 65 h. The mixture became homogeneous after a few hours but began to deposit crystals toward the end of the reaction period. The mixture was diluted with 25 mL of anhydrous ether, cooled briefly in an ice bath, and filtered. The crystals were washed with ether and dried under vacuum at 50 °C to give 4.05 g (99%) of the imidate, as the BF_4^- salt: mp 168–170.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.10 (m, 4 H), 4.37 (s, 3 H), 7.2–7.6 (m, 11 H); IR (KBr) 3200, 1683, 1647 cm^{-1}; MS, m/e (relative intensity) 251 (47), 174 (100).

Anal. Calcd for $C_{17}H_{17}NO$·HBF_4: C, 60.21; H, 5.25; N, 4.13; F, 7.90. Found: C, 60.02; H, 5.38; N, 4.14; F, 7.77.

3,5,6,7-Tetrahydro-5,5-diphenyl-2*H*-pyrrolo[1,2-*a*]imidazole (18). Imidate **17** was converted to its free base by shaking a methylene chloride suspension of the tetrafluoroborate salt with excess aqueous 1 M sodium hydroxide until disolution was complete. The methylene chloride layer was dried (K_2CO_3) and evaporated to give the imino ether, which was generally used immediately.

A solution of 1.56 g (6.21 mmol) of the imino ether and 1.30 g (6.28 mmol) of 99% bromoethylamine hydrobromide in 30 mL of methanol was heated at reflux for 23 h. After cooling, the reaction mixture was diluted with 150 mL of chloroform, washed with 25 mL of 1 M sodium hydroxide, dried ($MgSO_4$), and evaporated to give 2.0 g of a foam. This was chromatographed on silica gel, eluting with 2.5% triethylamine in methylene chloride, to give 0.95 g (58%) of **18** mp 141–144 °C. An analytical sample, mp 143–146 °C, was prepared by recrystallization from DMF–water: ^{1}H NMR ($CDCl_3$) δ 2.5–2.8 (m, 2 H), 2.8–3.15 (m, 4 H), 4.08 (br t, 2 H), 7.0–7.6 (m, 10 H); IR ($CHCl_3$) 1646 cm^{-1}; MS, m/e (relative intensity) 262 (21), 185 (100).

Anal. Calcd for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.34; H, 6.87; N, 10.68.

Acknowledgment. We thank the members of the Physical Chemistry Department, Hoffmann-La Roche, Inc., for microanalyses and spectal determinations and Dr. R. W. Kierstead for his support and encouragement.

Registry No. 1, 53267-01-9; **3a**, 54589-41-2; **3b**, 96306-54-6; **3b** (alcohol), 96306-72-8; **4a**, 96306-55-7; **4b**, 96306-56-8; (±)-*cis*-**5a**, 96306-57-9; (±)-*trans*-**5a**, 96306-58-0; (±)-*cis*-**5b**, 96306-59-1; (±)-*trans*-**5b**, 96306-60-4; (±)-*cis*-**6b**, 96306-62-6; (±)-*trans*-**6b**, 96306-63-7; (±)-**7a**, 96306-64-8; (±)-**7b**, 96306-65-9; (±)-**8**, 96306-66-0; (±)-**9**, 96306-61-5; (±)-**10**, 96326-01-1; (±)-**11**, 96306-67-1; (±)-**12**, 96306-68-2; **13**, 2426-87-1; **15**, 26004-45-5; **16**, 40052-79-7; **17**·HBF_4, 96306-70-6; **18**, 96306-71-7; BrPh, 108-86-1; *p*-$PhCH_2OC_6H_4CBPh$, 54589-41-2; $H_2NCH_2CH_2NH_2$·TsOH, 23571-07-5; $Br(CH_2)_2NH_2$·HBr, 2576-47-8; CH_2=CHCN, 107-13-1.

Supplementary Material Available: Tables listing the final atomic parameters, the final anisotropic thermal parameters, bond lengths, and bond angles for **9** (5 pages). Ordering information is given on any current masthead page.

Reactions of Ketenes with Sulfilimines. Synthetic Routes to Oxazolinones and Indolinones

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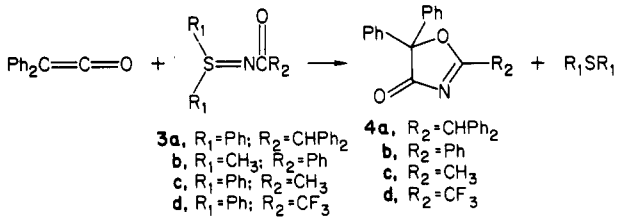
Received October 5, 1984

The reactions of diphenylketene and *tert*-butylcyanoketene with several sulfilimines were investigated. 5,5-Diphenyl-2-oxazolin-4-ones were produced from *N*-acylsulfilimines and diphenylketene while a 2-indolinone was obtained from *N*-arylsulfilimine and the same ketene. *tert*-Butylcyanoketene afforded either simple substituted or ortho-rearranged amides when *S*,*S*-dimethylsulfilimines were used as substrates. The structure of 2,5,5-triphenyloxazolidin-4-one (**7b**) was confirmed by single-crystal X-ray examination. Possible mechanistic pathways which account for all observed products are discussed.

Although the cycloaddition reactions of diphenylketene and *tert*-butylcyanoketene with allenes,[2a–c] alkynes,[3a–c] alkyl azides,[4] oxaziridines,[5a–c] olefins,[6a–c] diimides,[7a,b] ylids,[7a,8] enamines[7a–9] nitrones,[10a–c] imines,[11a–c] thiazoles,[12a,b] tertiary

0022-3263/85/1950-2224$01.50/0

Scheme I



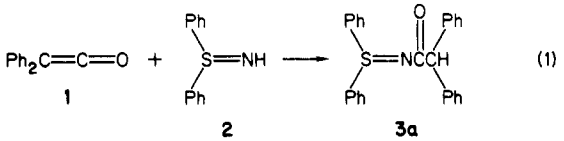
3a, R_1=Ph; R_2=$CHPh_2$
b, R_1=CH_3; R_2=Ph
c, R_1=Ph; R_2=CH_3
d, R_1=Ph; R_2=CF_3

4a, R_2=$CHPh_2$
b, R_2=Ph
c, R_2=CH_3
d, R_2=CF_3

amines,[13] and imino ethers[14] have been reported, the reactions of these ketenes with sulfilimines have not been fully explored.

As a continuation of our previous investigations of the reactions of ketenes with *N*-alkyl- and *N*-arylnitrones[15a,b] we have examined the reactions of diphenylketene and *tert*-butylcyanoketene with various sulfilimines.

Tomimatsu and co-workers[16] have reported that the reaction of equimolar amounts of diphenylketene (1) and diphenylsulfilimine (2) at 0 °C afforded the expected acylation product **3a** in 34% yield (eq 1).

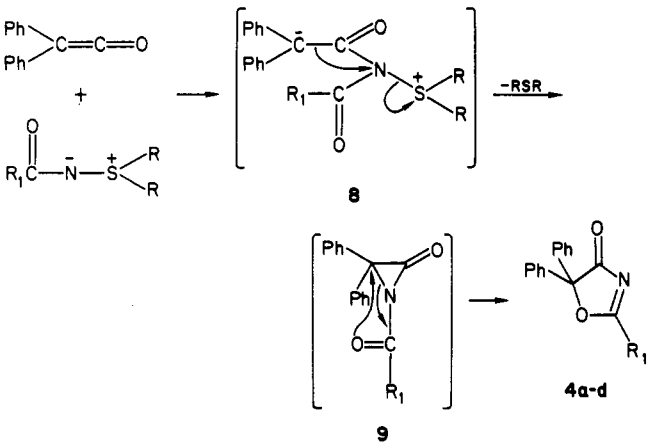


(1)

1 2 3a

These results are consistent with the fact that diphenylsulfilimine (2) is a relatively strong base (p*K*a ≃ 8.5)[17] and is readily acylated or alkylated with various electrophiles to afford the corresponding N-substituted sulfilimines.[18a,b] As sulfilimine **3a** still has a nucleophilic nitrogen,[19] we expected that this compound could react with an additional molecule of ketene if present and therefore we reinvestigated this reaction.

Scheme II



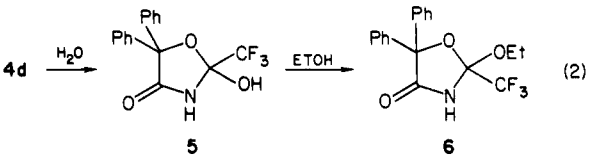
8 9 4a-d

Results and Discussion

The reaction of equimolar amounts of diphenylketene (1), and diphenylsulfilimine (2) at 0 °C afforded **3a** in 75% yield but with excess ketene, the intermediate **3a** reacted further to give **4a** and diphenyl sulfide. This reaction was extended to other *N*-acylsulfilimines and it was found to be a general method for the synthesis of 2-substituted 5,5-diphenyl-2-oxazolin-4-ones in high yields (Scheme I).

Electron-withdrawing groups on the sulfilimine nitrogen decrease the nucleophilicity of the nitrogen and accordingly decrease the reactivity of the sulfilimine. This is best exemplified by the fact that *S,S*-dimethyl-*N*-benzoylsulfilimine (**3a**) reacted completely with diphenylketene in refluxing toluene (4 h), whereas *S,S*-dimethyl-*N*-(4-nitrobenzoyl)sulfilimine was recovered unchanged after 24 h under the same conditions.

Oxazolinone (**4d**) could not be isolated since moisture rapidly added to the imino double bond to give **5**, reflecting the substantially enhanced electrophilic character at C-2 due to the electron-withdrawing effect of the trifluoromethyl group.[20] The structure of the tetrahedral species **5** was corroborated by its behavior in refluxing ethanol to afford 2-ethoxy-2-(trifluoromethyl)-5,5-diphenyl-4-oxazolidinone (**6**) (eq 2).



(2)

5 6

Compounds **4a–c** underwent selective hydride reduction of the imino double bond to afford the corresponding 4-oxazolidinones **7a–c**. This is in contrast to the catalytic hydrogenation of **4b** which produces a 3:1 mixture of *N,N*-diphenylacetylbenzamide[21] and the isomeric 4-oxazolidinone **7b**. The structure of **7b** was confirmed via single-crystal X-ray analysis. The geometry of the 4-oxazolidinone ring has been studied for a number of derivatives by both NMR[22] and CD[23] techniques. It has been

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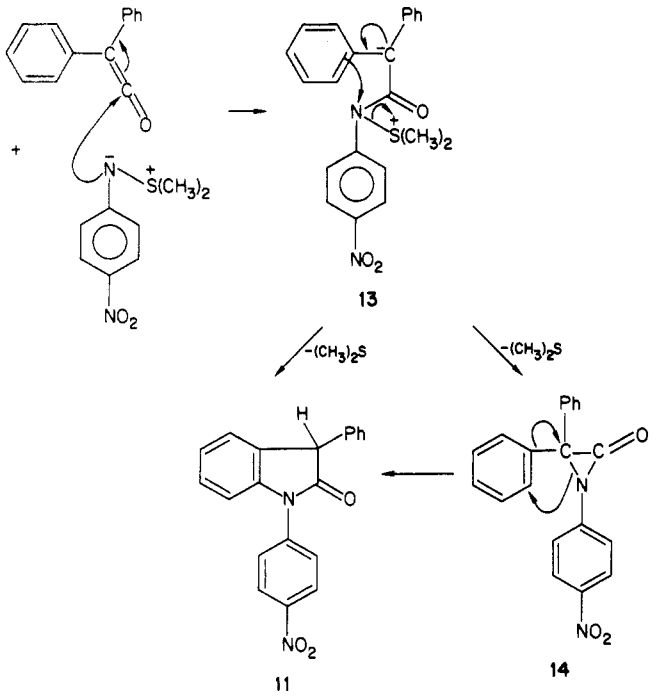
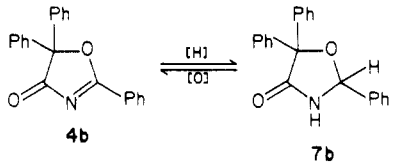
Scheme III



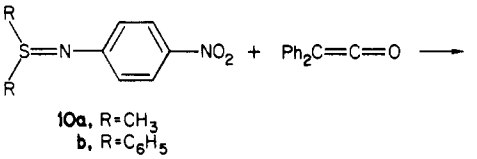
established that in solution, the ring usually assumes a preferred envelope conformation in which the three carbons and nitrogen are planar and the oxygen lies out of the plane. Furthermore, with bulky substituents at the 2- and 5- positions, the cis form, in which both groups are pseudoequatorial is expected to be the lower energy conformation, due to minimum steric nonbonded interactions and the X-ray analysis confirms this expectation for the 2-phenyl group in the solid state. Compounds **7b** and **7c** were synthesized independently by an alternate method.[24] Interestingly, **7b** can be reoxidized to its precursor **4b** with either DDQ or alternatively by sequential treatment with bromine and base (which presumably proceeds via elimination of hydrogen bromide from a transient *N*-bromo species) (eq 3).



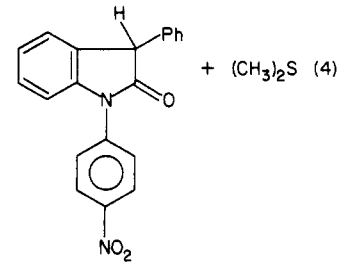
(3)

The formation of 2-oxazolinones **4a–d** from diphenylketene and *N*-acylsulfilimines can be rationalized in terms of known ketene chemistry, involving initial nucleophilic attack by the sulfilimine nitrogen on the ketene carbonyl. The delocalized zwitterion 8 thus produced may undergo cyclizaiton with the concomitant loss of dialkyl sulfide to afford an *N*-acyl α-lactam intermediate **9** which rearranges to **4** (Scheme II).

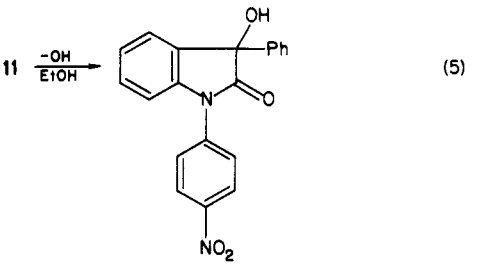
Reactions of Diphenylketene with *N*-Arylsulfilimines. Diphenylketene reacts readily with *S,S*-dimethyl-*N*-(*p*-nitrophenyl)sulfilimine (**10a**) with loss of dimethyl sulfide and formation of a complex mixture of products from which 1-(*p*-nitrophenyl)-3-phenyl-2-indolinone (**11**) was isolated as the major product (eq 4). In an attempt to improve the yield of **11** by eliminating the possibility of competing Sommelet–Hauser type rearrangement, *S,S*-diphenyl-*N*-(*p*-nitrophenyl)sulfilimine (**10b**) was allowed to react with diphenylketene; however, no improvement in yield was observed. Furthermore, indolinone (**11**) was found to undergo autoxidation in basic medium to afford 3-hydroxy derivative **12** (eq 5).



10a, R=CH_3
b, R=C_6H_5



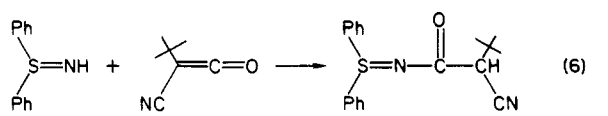
(4)



(5)

Several pathways may be postulated to account for the formation of **11**. An α-lactam intermediate has been invoked by Sheehan[25] to explain the formation of oxindole products arising from the reaction of 2-chloro-α,α-diphenylacetamide with sodium hydride. Accordingly, one likely pathway would involve attack by the sulfilimine nitrogen on the carbonyl of the ketene producing a delocalized zwitterion **13** which undergoes cyclization affording an α-lactam **14**, which subsequently rearranges to **11**. Alternatively, the same zwitterion **13** may cyclize directly to **11** via ortho attack on the sulfilimine nitrogen with loss of dimethyl sulfide (Scheme III).

Reactions of *tert*-Butylcyanoketene and Sulfilimines. The reaction of *tert*-butylcyanoketene (**15**) (TBCK), generated in situ from 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone, with *S,S*-diphenylsulfilimine (**2**) afforded the acylated product, *S,S*-diphenyl-*N*-α-*tert*-butylacetylsulfilimine (**16**) in 55% yield (eq 6). Although excess TBCK was used, no 2:1 adducts were identified from this reaction.



(6)

When *S,S*-dimethyl-*N*-benzoylsulfilimine (**3b**) was allowed to react with the same ketene, the major product isolated was *N*-benzoyl-α-*tert*-butyl-α-cyanoacetamide (**17**). Formation of this amide apparently proceeds through a Pummerer type reaction[26] involving internal hydrogen transfer in zwitterion **18** producing the ion pair **19**, which

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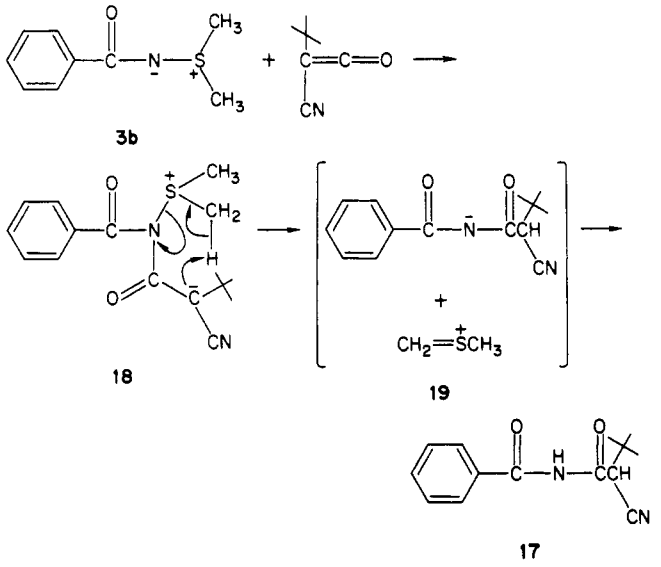
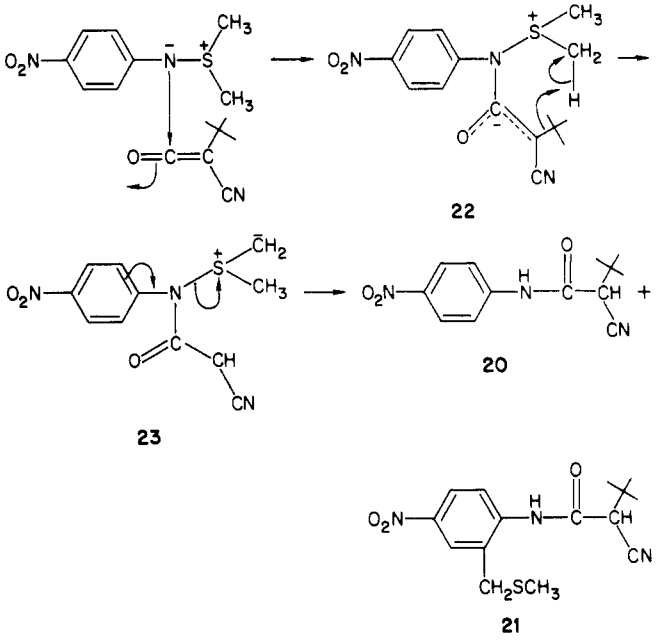
Scheme IV



Scheme V



dissociates to afford **17** (Scheme IV).

Finally, when TBCK and *S,S*-dimethyl-*N*-(*p*-nitrophenyl)sulfilimine (**10a**) were allowed to react in refluxing benzene, *N*-(4-nitrophenyl)-α-cyano-α-*tert*-butylacetamide (**20**) and the ortho-rearranged amide (**21**) were isolated in 22% and 33% yields, respectively. While the formation of **20** can be explined as arising from Pummerer type pathway as previously discussed, the *o*-(methylthio)methyl product **21** formation could be rationalized in terms of a Sommelet-Hauser type rearrangement.[27] In this case, internal hydrogen transfer from the methylthio group of zwitterion **22** produces the azasulfonium ylid **23** which undergoes a [2,3]sigmatropic rearrangement to afford **21** (Scheme V).

Experimental Section

N-acyl- and *N*-aryl-*S,S*-dimethylsulfilimines were prepared by condensation of the appropriately substituted amine with dimethyl sulfoxide activated with trifluoroacetic anhydride[28] or oxalyl chloride.[29] *S,S*-Diphenylsulfilimine monohydrate was purchased from Tridom-Fluka and was acylated according to the procedure of Oae.[18] Diphenylketene[30] and *tert*-butylcyanoketene[31] were prepared following reported procedures. Flash chromatography was performed using 40 μm silica gel (J. T. Baker Co.).

All melting points were determined on a Thomas-Hoover Unimelt apparatus and are uncorrected. Infrared spectra were recorded on a Pye-Unicam SP-1000 spectrophotometer. The ^1H NMR spectra were determined on a Perkin-Elmer R-32 (90 MHz) instrument. ^{13}C NMR spectra were determined on a Varian XL-100 (25.16 MHZ) instrument equipped with a Nicolet 1180 computer. Low-resolution mass spectra were obtained on a Perkin-Elmer-Hitachi RMU-6H spectrometer and exact mass measurements were taken on a VG 7070 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

***S,S*-Diphenyl-*N*-(trifluoroacetyl)sulfilimine (3d).** Trifluoroacetic anhydride (4 mL, excess) was added to a solution of diphenylsulfilimine (1.0 g, 4.5 mmol) in 125 mL of benzene at room temperature. The reaciton was stirred for 30 min, poured into a separatory funnel, washed with 150 mL of water (3 portions), dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure to afford a residual oil which crystallized upon the addition of hexane (15 mL). Filtration afforded pure **3d** as fluffy white needles (1.3 g, 92% yield): mp 85–86.5 °C; IR (KBR) $\nu_{C=O}$ 1640 cm^{-1}; mass spectrum, *m/e* 297 (M^+), 228 ($M^+ - CF_3$), 186. Anal. Calcd for $C_{14}H_{10}F_3NOS$: C, 56.56; H, 3.39; N, 4.71; F, 19.17. Found: C, 56.73; H, 3.44; N, 4.56; F, 18.91.

***S,S*-Diphenyl-*N*-(*p*-nitrophenyl)sulfilimine (10b).** *S,S*-Diphenylsulfilimine (0.8 g, 3.67 mmol) and 1-fluoro-4-nitrobenzene (excess) were refluxed for 24 h in benzene (20 mL). The solvent was removed under reduced pressure and the crude reaction mixture was applied to a silica gel column and eluted with 15% ethyl acetate/hexane to afford **10b** as yellow crystals (0.5 g, 38% yield): mp 131–133 °C; IR (KBR) 1590, 1575, 1480, 1260, 1010, 890 cm^{-1}; mass spectrum, *m/e* 332 (M^+). Anal. Calcd for $C_{18}H_{14}N_2O_2S$: C, 67.06; H, 4.37; N, 8.68; S, 9.94. Found: C, 66.85; H, 4.43; N, 8.68; S, 10.12.

Reactions of Diphenylketene with *N*-Acylsulfilimines. General Procedure for the Preparation of 2-Oxazolin-4-ones (4a–d). Diphenylketene (1.1 mol) was dissolved in the specified solvent and was added dropwise to a refluxing solution of the appropriately substituted sulfilimine (**3a–d**) in the same solvent. The reactions were monitored by TLC and when complete, the products were isolated by flash chromatography with a mixture of hexane/ethyl acetate. Oxazolinone, reaction solvent, melting point, and yield were as follows: **4a**, CH_2Cl_2, 162–164 °C, 73%; **4b** $C_6H_5CH_3$, 167–168 °C (lit.[24,32] 169 °C), 80%; **4c** (characterized as **7c**), CH_2Cl_2, 199–200 °C (lit.[31] 218–219), 56%; **4d** (characterized as **5**), xylene, 180–181.5 °C, 68%.

2-Ethoxy-2-(trifluoromethyl)-5,5-diphenyl-4-oxazolidinone (6). 2-Hydroxy-2-(trifluoromethyl)-5,5-diphenyl-4-oxazolidinone (**5**) (0.3 g, 0.77 mmol) was refluxed overnight in 25 mL of anhydrous ethanol. The solvent was removed under reduced pressure and pure **6** was isolated as white crystals (0.2 g, 66% yield, mp 147–149 °C, after flash chromatography with 15% ethyl acetate/hexane as eluent. IR (KBR) 3200, 1740, 1210 cm^{-1}; mass spectrum, *m/e* 351 (M^+), 306, 282, 183, 166, 105; ^1H NMR ($CDCl_3$) δ 8.4 (broad, NH), 7.8–7.2 (m, 10 H), 3.4 (q, 2 H), 1.2 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 173.11 (s, C=O), 114.81 (s, OCN)., Anal. Calcd for $C_8H_{16}NO_3F_3$: C, 61.54; H, 4.59; N, 3.99. Found: C, 61.45; H, 4.54; N, 4.01.

General Procedure for Hydride Reduction of 4a–c. Preparation of 4-Oxazolidinones (7a–c). Oxazolinones (**4a–c**) were dissolved in a minimum amount of isopropyl alcohol and stirred overnight with sodium borohydride (excess). The reaction mixture was acidified with acetic acid, diluted with water, and

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extracted with methylene chloride. The CH_2Cl_2 extract was dried and evaporated to afford the following oxazolidinones: **7a**, mp 210–212 °C (75%); **7b**, mp 162–164 °C (83%). Compounds **7a** and **7b** were also prepared with $LiAlH_4$ in THF in comparable yields to those of the $NaBH_4$ reduction.

Synthesis of Oxazolidinones by the Fisher Method. Benzilamide (5.0 g, 22 mmol) and the appropriate aldehyde (50 mmol) were heated with concentrated hydrochloric acid (4.15 mL, 50 mmol). After 1 h, water (75 mL) was added and the mixture was cooled in an ice bath until the oily residue completely solidified. Filtration afforded a white solid which was washed with water, dried, and recrystallized from ethanol. Oxazolidinones, aldehyde used, melting point, and yield were as follows: **7b**, benzaldehyde 161–162 °C, 66%; **7c**, acetaldehyde, 199–201 °C, 59%.

Bromine Oxidation of 7b. 2,5,5-Triphenyl-4-oxazolidinone (0.5 g, 1.6 mmol) and bromine (0.16 g, 3.1 mmol) were stirred in 15 mL of $CHCl_3$ for 2 h at room temperature, after which time 20% aqueous sodium hydroxide (20 mL) was added and the mixture stirred for an additional hour. The layers were separated and the aqueous layer was extracted with three 20-mL protions of $CHCl_3$. The combined organic layers wer then washed with two 50-mL portions of saturated aqueous sodium thiosulfate, 10% sodium bicarbonate (50 mL), and saturated brine (50 mL), dried with $MgSO_4$, and filtered. Removal of solvent and recrystallization of the residue from ethanol (5 mL) afforded pure **4b** (0.4 g, 77% yield), mp 167–168 °C). Compound **4b** was isolated in 95% yield with 2,3-dichloro-5,6-dicyanobenzoquinone in refluxing dioxane.

Reaction of Diphenylketene with 10a. 1-(4-Nitrophenyl)-3-phenyl-2-indolinone (11). *S,S*-Dimethyl-*N*-(*p*-nitrophenyl)sulfilimine **10a** (0.4 g, 2 mmol) and diphenylketene (0.5 g, 2.4 mmol) were refluxed for 2 h in 25 mL of benzene. (TLC indicated the absence of sulfilimine.) The solvent was removed under reduced pressure and the residue applied to a silica gel column to afford **11** as yellow crystals (0.4 g, 55.6% yield): mp 146–148 °C; IR (KBr) 1740, 1620, 1590, 1510, 1360, 1170 cm^{-1}; mass spectrum, *m/e* 330 (M^+), 301 (M^+ – HCO), 255, 225, 179, 165; ^1H NMR ($CDCl_3$) δ 8.5–7.7 (q, 4 H), 7.4–6.9 (m, 9 H), 4.85 (s, 1 H). Anal. Calcd for $C_{20}H_{14}N_2O_3$: C, 72.73; H, 4.24; N, 8.48. Found: C, 72.94; H, 4.44; N, 8.37.

Reaction of 11 with KOH. 1-(4-Nitrophenyl)-3-hydroxy-3-phenyl-2-indolinone (12). 2-Indolinone (**11**) (0.2 g, 0.6 mmol) and potassium hydroxide (0.2 g, excess) were dissolved in ethyl alcohol (20 mL) and stirred for 48 h. The solvent was removed under reduced pressure and water (10 mL) was added. The mixture was extracted with three (15-mL) portions of CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure and the residue separated by flash chromatography (10% ethyl acetate/hexane) to afford **12** as yellow crystals (0.1 g, 33% yield): mp 182–183 °C; IR (KBr) 3320, 1720, 1620, 1590, 1520, 1360 cm^{-1}; mass spectrum, *m/e* 346 (M^+), 317, 271, 195, 167, 166, 77; ^1H NMR δ 8.5–7.6 (q, 4 H, *J* 9 Hz, 19.8 Hz), 7.5–7 (m, 9 H), 5.3 (s, OH). Anal. Calcd for $C_{20}H_{14}N_2O_4$: C, 69.36; H, 4.05; N, 8.10. Found: C, 68.95; H, 4.32; N, 8.04.

Reaction of *tert*-Butylcyanoketene with 2. *S,S*-Diphenyl-*N*-(α-cyano-α-*tert*-butylacetyl)sulfilimine (16). 2,5-Diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (4.4 g, 145 mmol) was dissolved in 20 mL of benzene and refluxed for 30 min. *S,S*-diphenylsulfilimine (**2**) (0.3 g, 1.45 mmol) was dissolved in 10 mL of benzene and added to the solution. The reaction mixture was refluxed for an additional 30 min. The solvent was removed under reduced pressure and the residue applied to a flash column and eluted with 25% ethyl acetate/hexane. The major fraction (R_f 0.38, 1:1 ethyl acetate/hexane) was isolated as a yellow oil which afforded white crystals (0.3 g, 55% yield), mp 96–98 °C upon trituration with ether. Recrystallization from 5 mL of ether gave pure **16**: mp 98–101 °C; IR (KBr) 2400 (C≡N), 1610 (C=O), 1290, 830 cm^{-1}; mass spectrum *m/e* 324 (M^+), 268, 228 (M^+ – $CH(CN)C(CH_3)_3$), 186, 171, 152, 117, 109, 77, 65, 57; ^1H NMR ($CDCl_3$) δ 1.2 (s, 9 H), 3.35 (s, 1 H), 7.4–7.8 (m, 10 H). Anal. Calcd for $C_{10}H_{20}N_2OS$: C, 70.34; H, 6.21; N, 8.63. Found: C, 70.35; H, 6.21; N, 8.60.

Reaction of *tert*-Butylcyanoketene with 3b. *N*-Benzoyl-α-cyano-α-*tert*-butylacetamide (17). *S,S*-Dimethyl-*N*-benzoylsulfilimine (**3b**) (0.5 g, 2.9 mmol) and 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (0.9 g, 2.9 mmol) were dissolved in 50 mL of toluene and refluxed for 18 h. TLC indicated some unreacted sulfilimine. The solvent was removed under reduced pressure and the residue applied to a silica gel column and eluted with 10% ethyl acetate/hexane to afford **17** as white crystals (0.2 g, 25% yield): mp 132–135 °C; IR (KBr) 3300 (NH), 2280 (C≡N), 1730 and 1700 (C=O); mass spectrum, *m/e* 245 ($M^+ + 1$), 229, 188, 105, 77; ^1H NMR ($CDCl_3$) δ 10.2 (s, 1 H, exchange with D_2O), 8.2–7.4 (m, 5 H), 5.0 (s, 10 H), 1.25 (s, 9 H). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 69.03; H, 675; N, 11.34.

Reaction of *tert*-Butylcyanoketene with 10a. *S,S*-Dimethyl-*N*-(4-nitrophenyl)sulfilimine (**10a**) (0.5 g, 2.75 mmol) and 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (0.5 g, 1.83 mmol) were refluxed for 4 h in benzene. The solvent was removed under reduced pressure and the residue separated by column chromatography (silica, 10% ethyl acetate/hexane) to afford two major products. *N*-(4-Nitrophenyl)-α-cyano-α-*tert*-butylacetamide (**20**) was isolated as a slightly yellowish powder (0.2 g, 22.3): mp 192–193 °C; IR (KBr) 3330, 2250, 1710, 15208 1350 cm^{-1}; mass spectrum, *m/e* 261 (M^+), 205, 138, 82, 57; ^1H NMR ($CDCl_3$) δ 9.0 (NH), 8.3–7.8 (q, arom), 307 (s, 1 H), 1.2 (s, 9 H). Anal. Calcd for $C_{13}H_{15}N_3O_3$: C, 59.73; H, 5.78; N, 16.08. Found: C, 59.60; H, 5.83; N, 16.04.

N-[(2-(Methylthio)methyl-4-nitrophenyl)]-α-cyano-α-*tert*-butylacetamide (**21**) was also isolated as slightly yellowish needles (0.3 g, 36% yield): mp 128–130 °C; IR (KBr) 3320, 2220, 1670, 1540, 1520, 1360 cm^{-1}; mass spectrum, *m/e* 321 (M^+), 306, 218, 151, 57; ^1H NMR ($CDCl_3$) δ 9.2 (NH), 8.4–8 (m, 3 H), 3.85 (s, 2 H), 3.4 (s, 1 H), 2.1 (s, 3 H), 1.3 (s, 9 H). Anal. Calcd for $C_{15}H_{19}N_3O_3S$: C, 56.07; H, 5.99; N, 13.07; S, 9.96. Found: C, 56.10; H, 6.00; N, 123.77; S, 9.88.

X-ray Structural Data. 2,5,5-Triphenyloxazolidin-4-one (7b) ($C_{21}H_{17}NO_2$, M_r = 315.37) is orthorhombic: space group $P2_12_12_1$, a = 12.185 (3) Å, b = 24.481 (3) Å, c = 11.002 (3) Å, v = 3287.9 (1.3) Å^3, Z = 8 (2 molecules in the asymmetric unit), d_{calcd} = 1.274 g cm^{-3}, $F(000)$ = 1328 electrons, μ(Cu) = 5.71 cm^{-1}, δ = 0.012, crystal size 0.25 × 0.45 × 0.55 mm. Six strong reflections affected by secondary extinction ($F_{obsd} \geq 120.9$) were omitted from the final structure refinement. The final residuals for 3398 data are R_{obsd} = 0.038, wR_{obsd} = 0.048, R_{all} = 0.038, wR_{all} = 0.048. The final difference Fourier map had p_{max} = 0.19 e/Å^3.

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Supplementary Material Available: A description of the X-ray structure experimental, solution, and refinement procedures, diagrams showing atomic numbering, tables of atomic parameters, bond distances, and angles for **7b**, least-squares best plane data, and a short description of intermolecular hydrogen bonding for **7b** (12 pages). Ordering information is given on any current masthead page.