unity, perhaps because of a decrease in hyperconjugative stabilization when a β-hydrogen is replaced by a methyl group.[11]

Moreover, the methyl effects depend on the solvent for sulfenylation[13] and bromination (Table II) and on the acidity for hydration.[8,12] These ratios are also very sensitive to steric factors, as is shown by the effect of a *cis*-β-methyl or a *tert*-butyl group, and this sensitivity depends on the size of the entering electrophile. These observations do not detract from the methyl effect method but underline that strict control of reaction parameters is essential. A critical application of this method, based on a comparison of ring substituent effects on styrene and α-methylstyrene bromination and designed to detect eventual bromine bridging, is in progress.[14]

Experimental Section

Bromination Kinetics. Two different methods both using TFCR-EXSEL conditions (very low concentrations in reagents—salt excess) have been used: couloamperometry[15] for rate constants above 5×10^3 M^{-1} s^{-1} and spectroscopy[16] for rate constants below this limit. In the couloamperometric method, bromine is produced in situ by electrolysis of NaBr; its uptake is followed by the decrease in the bromine diffusion current between two Pt electrodes. Second-order conditions (first order in bromine and in olefin) are used: the bromine concentration is in the range 10^{-5}–10^{-7} M and the initial olefin concentration is approximately half this. In the UV spectroscopic method, bromine (10^{-3}–10^{-4} M overall) is syringed into the reaction cell and its consumption is followed by the absorbance change at a fixed wavelength (280–320 m).

In both methods, reproducibility is within 2%.

Rate Constants for Free Bromine Addition. In acetic acid and in methanol, direct measurement of these constants in the absence of bromide ion is not possible for technical reasons: in couloamperometry, a bromide salt is necessary to produce bromine; in spectroscopy, the absorption coefficient of free bromine is too small for accurate determinations in very dilute solutions. Moreover, bromide ions are produced during the bromination in the reaction pathway leading to solvent incorporated products. These ions give, via the equilibrium

$$Br_2 + Br^- \overset{K}{\rightleftharpoons} Br_3^-$$

the electrophilic tribromide ions addition which competes with that of free bromine. This time-dependent competition leads to erratic kinetics. Consequently, rate measurements are always made with an excess of bromide ion. Free bromine rate constants are, then, obtained by means of eq 1 from k_{exp} measured at several bromide ion concentrations. Plotting $k_{exp}(1 + K[Br^-])$ against $[Br^-]$ gives a straight line whose origin is k_{Br_2}.

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Heterocycles from Ketenimines. 12.[1] Pyrrolo[3,2-*b*]pyridines

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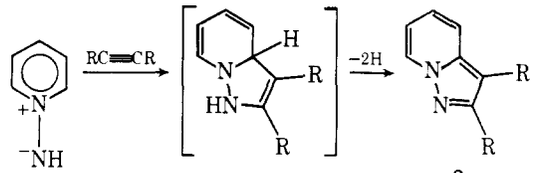
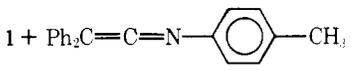
The cycloadducts formed from the reactions of pyridine-*N*-imines and 1,3-dipolarphiles usually are unstable and undergo rapid dehydrogenation to the aromatic pyrazolopyridine system **2**.[2] We now describe the reaction of pyridine-*N*-imines with triarylketenimines.



1 2

From the reaction of equimolar concentrations of 1 and diphenylketene-*N*-*p*-tolylimine (**3**) was isolated a 54% yield of a bright orange solid **4**. Structural assignment of 4 as 2,3-



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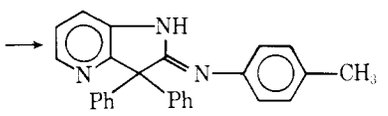

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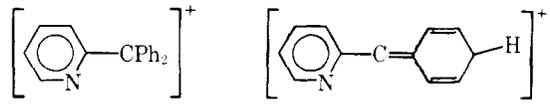
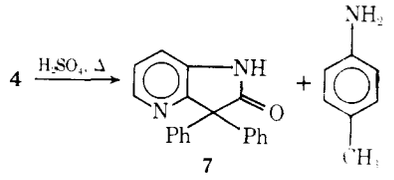
dihydro-3,3-diphenyl-2-(*p*-tolylimino)-1*H*-pyrrolo[3,2-*b*]-pyridine is based on composition: IR absorption at 1590 cm^{-1} (imine stretch); NMR absorptions at δ 2.28 (methyl group) and 7.0–8.5 (the aromatic protons and the amidine N–H); and MS fragments at *m/e* 375 (parent ion), 244 (**5**), and 167 (**6**).



5 6

Chemical evidence to support the assigned structure of 4 was obtained from two reactions. Hydrolysis of 4 with hot sulfuric acid gave 3,3-diphenyl-4-azaoxindole (**7**) and *p*-toluidine. This azaoxindole was identified by IR (absorption at 1665 cm^{-1} for the amide carbonyl), NMR (absorptions from δ 7.0–8.5 for the aromatic and the amide N–H protons),



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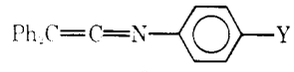
high-resolution MS, and MS (the parent ion at m/e = 286, **5** and **6**).

Additional evidence for **4** was gained from the reaction of **3** with pyridine-d_5-*N*-imine. Since pyridine-*N*-imine is generated from the amine salt with sodium methoxide, one would anticipate that the alkaline conditions would result in exchange of the pyridine's deuteriums. The 2, 4, and 6 positions of the pyridine ring should undergo exchange, although at different rates, while the 3 and 5 positions should not exchange.[3] Thus, the minimum atoms of deuterium still incorporated in each imine molecule under these conditions should be two. The structure proposed for **4** would require displacement of the deuterium atom at the 3 position of the imine. Therefore, adducts from **3** and pyridine-d_5-N-imine should be obtained which contain one deuterium (at position 6), two deuteriums (at positions 5 and 6 or 6 and 7), and three deuteriums (at positions 5, 6, and 7). Ions (in the MS) of 376 (375 + 1 D), 377 (375 + 2 D), and 378 (375 + 3 D) were observed.[4]

Steric problems are not important in this cycloaddition from the standpoint of ketenimine structure[5] as evidenced by the success of the reaction with diphenylketene-*N*-(2,6-dimethylphenyl)imine. Consistent with the course of the reaction 2-picoline-*N*-imine did undergo cycloaddition with **3** while 2,6-lutidine-*N*-imine would not (only hydrolysis of **3** to its amide was observed). Thus, the only steric problem associated with the cycloaddition occurs when both the 2 and 6 positions of the pyridine-*N*-imine are substituted.

Since some reactions of diphenylketene N-para-substituted phenylimines have been shown to be sensitive to the electronic character of the para substitutent,[6] the reaction was studied with **8** where Y was methoxy, methyl, hydrogen, fluoro, and iodo. Under identical conditions of temperature and time, the



8

reactions of the various substituted ketenimines with pyridine-*N*-imine gave comparable isolated yields. Interestingly, when 2-bromopyridine-*N*-imine was employed with **3**, no adduct was formed.

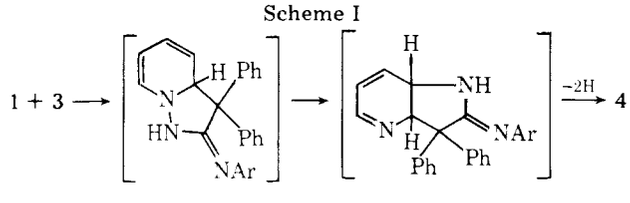
Scheme I outlines a plausible mechanism to account for the products and observations. The steps are an initial 1,3-dipolar cycloaddition followed by a 1,5-sigmatropic rearrangement with the subsequent loss of two hydrogens.[7]

Experimental Section

NMR spectra were determined on a Jeolco Minimar spectrometer. Tetramethylsilane was used as the internal standard and chloroform-*d* or acetone-d_6 was used as solvent. IR were determined with a Perkin-Elmer Model 137B or a Perkin-Elmer Model 137G spectrophotometer. The spectra of solids were obtained by incorporating the sample into a pellet of potassium bromide. The band at 1603 or 2933 cm^{-1} of a polystyrene film (0.05 mm) was used as a reference peak. MS were recorded on a Hewlett-Packard Model 5920 spectrometer while the high-resolution MS was determined by the Department of Chemistry, Massachusetts Institute of Technology. Elemental analyses were performed by the Heterocyclic Chemical Corporation of Harrisonville, Mo. Melting points were determined on a Meltemp apparatus and are uncorrected.

2,3-Dihydro-3,3-diphenyl-2-(*p*-tolylimino)-1*H*-pyrrolo[3,2-*b*]pyridine (4). Ten grams of sodium methoxide (0.18 mol) was added to 300 mL of isopropyl alcohol while the solution was being stirred. This solution was cooled to 0 °C in an ice bath, and, while the solution was stirred, 2.83 g (0.01 mol) of diphenylketene-*N*-*p*-tolylimine and 2.2 g (0.01 mol) of *N*-aminopyridinium iodide were added. The solution was stirred for 1 h and poured into 300 mL of cold water and the resulting precipitate was collected. The precipitate was dissolved in 100 mL of $CHCl_3$, dried with $MgSO_4$, treated with decolorizing carbon, and then concentrated in vacuo. The solid that remained was treated with two 100-mL portions of pentane to remove any unreacted ketenimine and then recrystallized from $CHCl_3$. A 40% yield (1.5 g) of a bright orange solid was collected: mp 216–217 °C; IR 3500 (w), 3000 (w), 1610 (s), 1590 (s), 1490 (m), 1300 (m), 1200 (m), 1150 (m), 1100 (w), 840 (m), 745 (m), and 700 (m) cm^{-1}; NMR δ 2.28 (s, 3 H), and 7.0–8.5 (m, 18 H); MS m/e 374 (25), 244 (100), 243 (45), 167 (25). When the reaction was performed at room temperature, a 54% yield was obtained.

Scheme I



Anal. Calcd for $C_{26}H_{21}N_3$: C, 83.20; H, 5.64; N, 11.20. Found: 83.12; H, 5.81; N, 11.31.

Hydrolysis of 2,3-Dihydro-3,3-diphenyl-2-(*p*-tolylimino)-1*H*-pyrrolo[3,2-*b*]pyridine. Preparation of 7. A solution of 1 g of **4** (0.0027 mol) in 50 mL of 50% H_2SO_4 was heated for 1 week. The solution was then cooled in an ice bath, made basic with $NaHCO_3$, and extracted with two 25-mL portions of $CHCl_3$. The $CHCl_3$ extract was dried with $MgSO_4$, treated with decolorizing carbon, and concentrated in vaccuo. The residue was recrystallized from acetonitrile to give 0.76 g (86% yield) of 3,3-diphenyl-4-azaoxindole (**7**): mp 214 °C; IR 1665 (s), 1300 (s), 1150 (s), and 700 (s) cm^{-1}; NMR δ 7.0–8.5 (m); MS m/e 286 (25), 244 (100), 243 (40), and 167 (30).

Anal. Calcd for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.90; N, 9.80. Found: C, 79.25; H, 4.52; N, 9.32. MS. Calcd for $C_{19}H_{14}N_2O$, 286.11061. Found, 286.11040.

The acetonitrile solvent was removed from the solution and the oil that remained was dissolved in 50 mL of pentane. Hydrogen bromide (prepared by adding concentrated H_2SO_4 to triethylamine hydrobromide) was bubbled through the pentane solution. A small amount of white precipitate formed and was collected. Its IR was superimposable with that from an authentic sample of *p*-toluidine hydrobromide.

Preparation of Adducts from Ketenimines and Pyridine-*N*-imines. All reactions were performed under the same conditions as for the preparation of **4** from **1** and **3** except that all were performed at room temperature rather than 0 °C.

From Pyridine-*N*-imine and Diphenylketene-*N*-(2,6-dimethylphenyl)imine. A 36% yield of adduct was obtained: mp 265–266 °C; IR 3010 (w), 1640 (s), 1600 (m), 1550 (m), 1425 (s), 1300 (m), 1140 (s), 1050 (w), 980 (m), 910 (w), 880 (m), 780 (s), 760 (s), 740 (m), and 700 (s) cm^{-1}; NMR δ 2.3 (s, 6 H), and 7.0–8.5 (m, 17 H); MS m/e 389 (56), 388 (24), 244 (100), 243 (35), 167 (25).

Anal. Calcd for $C_{27}H_{23}N_3$: C, 83.29; H, 5.91; N, 10.80. Found: C, 83.12; H, 5.86; N, 10.53.

From Pyridine-d_5-*N*-imine and 3. A 30% yield of products was obtained which had the following properties: mp 209–212 °C; IR 3010 (w), 1610 (w), 1590 (s), 1530 (m), 1490 (m), 1300 (m), 1270 (m), 1250 (m), 1120 (s), 1100 (s), 1050 (w), 990 (w), 840 (w), 750 (s), 700 (s) cm^{-1}; NMR δ 2.28 (s, 3 H) and 7.0–8.5 (m, 16.6 H); MS m/e 378 (50), 377 (75), 376 (75), 375 (25), 247 (75), 246 (100), 245 (90), 244 (30), 169 (20).

From 2-Picoline-*N*-imine and 3. A 77% yield of adduct was obtained: mp 256–257 °C; IR 3010 (w), 1610 (w), 1590 (s), 1550 (s), 1510 (m), 1475 (m), 1400 (w), 1300 (m), 1250 (m), 1150 (s), 1090 (w), 1050 (w), 957 (m), 825 (m), 760 (m), and 700 (w) cm^{-1}; NMR δ 2.28 (s, 3 H), 2.68 (s, 3 H), and 7.0–7.7 (m, 17 H); MS m/e 389 (100), 388 (60), 256 (75), 255 (30), and 181 (18).

Anal. Calcd for $C_{27}H_{23}N_3$: C, 83.30; H, 5.92; N, 10.80. Found: C, 83.09; H, 6.06; N, 10.59.

From 1 and Diphenylketene-*N*-*p*-anisylimine. A 40% yield of the adduct was obtained: mp 196–197 °C; IR 3010 (w), 1630 (m), 1600 (m), 1550 (s), 1500 (s), 1450 (s), 1300 (m), 1250 (m), 1175 (m), 1150 (s), 1050 (m), 980 (w), 840 (m), 760 (s), 750 (m), and 700 (m) cm^{-1}; NMR δ 3.72 (s, 3 H) and 6.2–8.5 (m, 18 H).

Anal. Calcd for $C_{26}H_{21}N_3O$: C, 79.77; H, 5.41; N, 10.73. Found: C, 79.45; H, 5.72; N, 10.48.

From 1 and Diphenylketene-*N*-phenylimine. The adduct was obtained in 45% yield: mp 224–225 °C; IR 3010 (s), 1650 (m), 1600 (s), 1550 (s), 1500 (s), 1450 (s), 1300 (s), 1175 (m), 1150 (s), 980 (m), 900 (w), 760 (s), 740 (w), and 700 (s) cm^{-1}; NMR δ 7.0–8.5 (m).

Anal. Calcd for $C_{25}H_{19}N_3$: C, 83.08; H, 5.30; N, 11.63. Found: C, 83.38; H, 5.48; N, 11.32.

From 1 and Diphenylketene-*N*-*p*-fluorophenylimine. The adduct was obtained in 43% yield: mp 249–250 °C; IR 3010 (w), 1625 (s), 1550 (s), 1500 (s), 1450 (s), 1300 (m), 1190 (s), 1150 (s), 980 (m), 880 (m), 850 (s), 760 (s), 730 (m), and 700 (m) cm^{-1}; NMR δ 6.7–8.5 (m).

Anal. Calcd for $C_{25}H_{18}N_3F\cdot H_2O$: C, 75.55; H, 5.07; N, 10.57. Found: C, 75.89; H, 4.83; N, 10.64.

From 1 and Diphenylketene-*N*-*p*-iodophenylimine. The adduct was obtained in 50% yield: mp 249–251 °C; IR 3010 (w), 1625 (s), 1560 (m), 1540 (s), 1490 (m), 1435 (m), 1300 (m), 1140 (s), 1000 (w), 950 (w), 840 (m), 760 (m), 750 (s), 735 (w), 710 (w), 700 (m) cm^{-1}; NMR δ 6.8–8.5 (m).

Anal. Calcd for $C_{25}H_{18}N_3I\cdot\frac{1}{2}H_2O$: C, 60.49; H, 3.79; N, 8.47. Found: C, 60.49; H, 3.86; N, 8.47.

Reaction of 2-Bromopyridine-*N*-imine with 3. From these reagents using similar quantities and conditions for the other reactions, only diphenyl *N*-*p*-tolylacetamide (the amide corresponding to **3**) was isolated.

Acknowledgment. The high-resolution mass spectrum was furnished by Dr. Catherine Costello of the National Institutes of Health facility of the Department of Chemistry at the Massachusetts Institute of Technology through NIH grant No. RR00317 with K. Biemann as the principal investigator.

Registry No.—**1**, 25275-41-6; **3**, 5110-45-2; **4**, 69027-81-2; **7**, 69027-82-3; **8** (Y = OMe), 40012-82-6; **8** (Y = H), 14181-84-1; **8** (Y = F), 41563-37-5; **8** (Y = I), 69027-83-4; *N*-aminopyridinium iodide, 6295-87-0; diphenylketene-*N*-(2,6-dimethylphenyl)imine, 42549-11-1; pyridine-d_5-*N*-imine, 69027-84-5; 2-picoline-*N*-imine, 51135-75-2; 2,3-dihydro-3,3-diphenyl-2-(2,6-dimethylphenylimino) -1*H*-pyrrolo[3,2-*b*]pyridine, 69027-85-6; 2,3-dihydro-3,3-diphenyl-2-(*p*-tolylimino)-1*H*-pyrrolo[3,2-*b*]-d_3-pyridine, 69027-86-7; 2,3-dihydro-3,3-diphenyl-5-methyl-2- (*p*-tolylimino)-1*H*-pyrrolo[3,2-*b*]pyridine, 69027-87-8; 2,3-dihydro-3,3-diphenyl-2-(*p*-anisylimino)-1*H*-pyrrolo[3,2-*b*]pyridine, 69027-88-9; 2,3-dihydro-3,3-diphenyl-2-(phenylimino)-1*H*-pyrrolo[3,2-*b*]pyridine, 69027-89-0; 2,3-dihydro-3,3-diphenyl-2-(*p*-fluorophenylimino)-1*H*-pyrrolo[3,2-*b*]pyridine, 69027-90-3; 2,3-dihydro-3,3-diphenyl-2-(*p*-iodophenylimino)-1*H*-pyrrolo[3,2-*b*]pyridine, 69027-91-4; 2-bromopyridine-*N*-imine, 69027-92-5.

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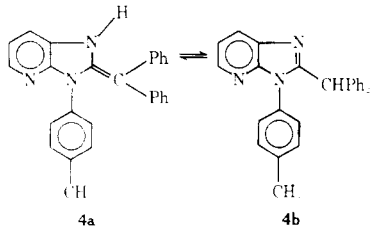
(4) One reviewer suggested that structures **4a** and **4b** were consistent with the data and should have been observed. We did not observe these compounds.



4a 4b

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Oxythioacetyl Chloride

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Received September 27, 1978

King and Durst[1] first clearly established the existence of the oxythioacyl chlorides, having isolated and established the structure of both geometric isomers of oxythiobenzoyl chloride (**1**). Other aryl derivatives as well as some complex, sterically hindered aliphatic analogues are also known but simple aliphatic derivatives have not yet been reported in spite of their possible synthetic utility.[2] In connection with current work

1 2

on the synthesis of alkyl-substituted thiirene oxides[3,4] we had occasion to examine the synthesis of the acetyl analogue **2**. Although **2** could be generated in ether solution at −30 °C by dehydrochlorination of sulfinyl chloride **4** according to the method devised by Strating, Thijs, and Zwanenburg[5] for compound **1** (see Scheme I), isolation of the pure substance proved to be impossible.[6]

The structure of **2** was established by its reaction with chlorine to give α,α'-dichloroethanesulfinyl chloride (**5**) which itself was identified by oxidation to the corresponding sulfonyl chloride **6**. The latter was unambiguously synthesized by oxidation of α,α'-dichloroethanesulfenyl chloride (**7**), the chlorinolysis product of ethyl dithioacetate (**8**). Sulfinyl chloride (**4**) was identified by comparison with spectral data kindly provided by King[7] who obtained it by treatment of the corresponding sulfinic acid with thionyl chloride. Oxythioacetyl chloride (**2**) did not react with diazomethane at low temperatures and above room temperature underwent spontaneous decomposition. With 1 phenyldiazomethane gave not the expected episulfoxide but instead 2,5-diphenyl-1,3,4-thiadiazole.[4,8]

Experimental Section[9]

1-Chloroethanesulfenyl Chloride (3). 1-Chloroethanesulfenyl chloride can be obtained in yields of 3–30% by chlorination of a solution of trithioacetaldehyde in CH_2Cl_2 at −10 °C.[10] A superior preparation was adapted from a more recent general method of Douglass and co-workers.[11] A solution of 30 g (0.25 mol) of ethyl disulfide in 400 mL of pentane was placed in a 1-L three-neck flask equipped with a mechanical stirrer, gas in- and outlet tubes, and a low-temperature thermometer. After cooling to −60 °C in a dry ice–acetone bath a gentle stream of Cl_2 was flashed over the surface of the vigorously stirred solution by evaporation of 53 g (0.76 mol) of precondensed chlorine. After the addition of Cl_2 was completed, the thick slurry of white crystals was slowly warmed to room temperature. Vigorous stirring was essential due to the evolution of HCl at the decomposition temperature of the sulfur trichloride (ca. 13 °C). Following decomposition the solvent was removed with a water aspirator from a water bath and the residual yellow-orange oil distilled to give 50.9 g (78%) of the sulfenyl chloride as a yellow-orange liquid: bp 49 °C (40 mm) (lit.[10b] bp 47–50 °C (40 mm)); NMR ($CDCl_3$) δ 1.88 (d, 3, CH_3), 5.40 (q, 1, CH).

1-Chloroethanesulfinyl Chloride (4). 1-Chloroethanesulfinyl chloride was prepared by adaptation of a method of Douglass and co-workers.[12] Freshly prepared 1-chloroethanesulfenyl chloride (50.9 g, 0.39 mol) was mixed with 40.0 g (0.39 mol) of acetic anhydride in a 250-mL three-neck flask equipped with a gas dispersion tube, a $CaCl_2$ drying tube, a low-temperature thermometer, and a magnetic

Scheme I