Reaction of *N*-(*p*-Tolylsulfonyl)diphenylcyclopropenimine with Pyridinium and Isoquinolinium Ylides

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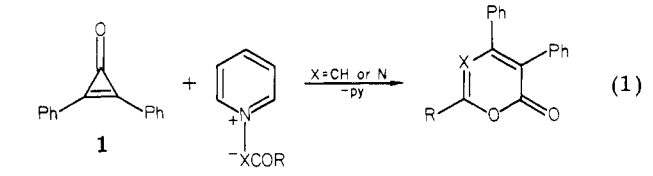
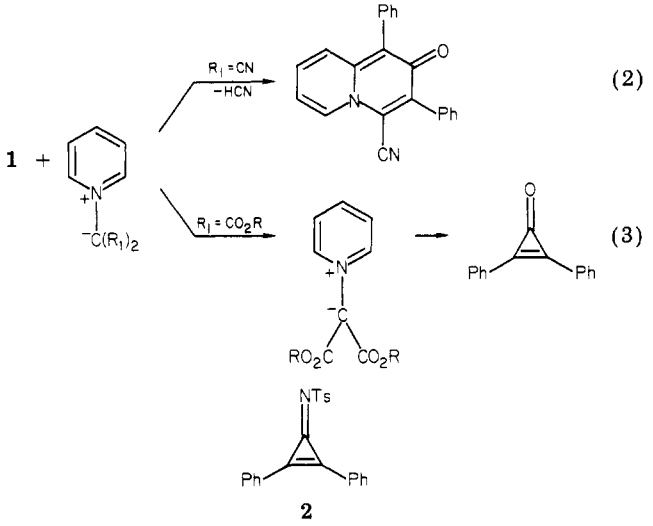
N-(*p*-Tolylsulfonyl)diphenylcyclopropenimine (**2**) reacted smoothly with pyridinium *N*-carbethoxyamide (**3**) to afford a new ylide (**5**), in addition to stilbene **4**, uracil **6**, and pyrimidinone **7**. An observed thermal transformation of **5** to **6** and **7** is discussed. Reaction of the cyanocarbethoxy methylides **15a–c** with **2** produced the internal salts **16a–c**, while the dicarbethoxy, monocarbethoxy, and benzoyl methylides **15d–f** gave the pyridine-free cyclics **26**, **28**, and **29**, respectively. The isoquinolinium methylides **31a–c** reacted in an analogous fashion, while the *N*-amides **33a,b** afforded cycloadducts **34a,b**. A series of reactions used to correlate the structures of the latter is described, including an observed cycloaddition mode for diphenylcyclopropenone (**1**) with **33a–c** which yielded **39**, **37**, and **42**, respectively.

While the chemistry of diphenylcyclopropenone (**1**) has received considerable attention in the recent literature,[1] that of nitrogen analogues [i.e., *N*-(*p*-tolylsulfonyl)diphenylcyclopropenimine (**2**)[2]] has been largely ignored. In particular, reaction of a variety of monosubstituted pyridinium *N*-amides[3] and pyridinium methylides[4] has been reported only for **1** (eq 1), the products in all cases being



(1)



(2)

(3)

2

consistent with a pathway involving initial nucleophilic attack on the cyclopropenone ring with subsequent elimination of pyridine. Recently, the reaction of **1** with pyridinium dicyanomethylide has been reported to furnish a product of 1,3-dipolar cycloaddition (eq 2),[5] while a charge-transfer complex has been isolated in the reaction with dicarboalkoxymethylides (eq 3).[6] The present study was undertaken with the objective of comparing the reactivity of diphenylcyclopropenimines, i.e., **2**, in reactions with mono- and disubstituted pyridinium and isoquinolinium ylides.

Table I. Product Distribution[a] from the Reaction of **2** with **3** in Benzene

molar ratio of 2/3	distribution, %				
	5	**4**	**6**	**7**	total
1:1	25	35	13	5	78
1:2	44	23	16	5	88
1:2[b] (with py)	25	30	20		75

[a] ±3%. [b] 2 mmol of pyridine added for 1 mmol of **2**.

Results and Discussion

(A) Reaction of 2 with Pyridinium *N*-Carbethoxyamide (3). While reaction of **1** with **3** was observed to proceed smoothly at room temperature,[3] that of **2** with **3** required 6 days in benzene under reflux conditions to assure total consumption of **2**. The results are summarized in Scheme I and Table I. All products were separated by means of column chromatography on silica gel (see Experimental Section). Initially, the reaction of equimolar quantities of reagents was examined, the major product in this case being 1-cyano-2-(*p*-tolylsulfonyl)-*trans*-stilbene (**4**), which has been previously isolated[7] from the reaction of **2** with triphenylphosphine. A second principal product, which was shown by elemental analysis and ^{1}H NMR integration to correspond to a 1:2 adduct less one pyridine nucleus, was assigned structure **5** on the basis of the appearance of two equivalent carbethoxy groups in the ^{1}H and ^{13}C NMR spectra and IR absorption at 1785, 1760, and 1710 cm^{-1}, in conjunction with an interesting thermal reaction observed for the system. Thus, a toluene solution of **5** that had been heated under reflux during 4 days afforded **3** (19%),[8] a uracil derivative **6** (28%), and the pyrimidinone **7** (41%), the latter two being other products isolated from the reaction of **2** with **3** (Table I). Both **6** and **7** were readily transformed to the known 5,6-diphenyluracil (**8**), the 2-ethoxy-4-pyrimidinone **9** appearing as an intermediate in the two-step hydrolysis of **7**.

(1) For reviews, see T. Eicher and J. L. Weber, *Top. Curr. Chem.*, **57**, 1 (1975); K. T. Potts and J. S. Baum, *Chem. Rev.*, **74**, 189 (1974).
(2) L. A. Paquette, T. J. Barton, and N. Horton, *Tetrahedron Lett.*, 5039 (1967).
(3) T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, **36**, 2451 (1971).
(4) T. Eicher and A. Hansen, *Tetrahedron Lett.*, 1169 (1967).
(5) K. Matsumoto and Y. Kono, *J. Chem. Soc., Chem. Commun.*, 1045 (1976).
(6) K. Matsumoto, H. Fujita, and Y. Deguchi, *J. Chem. Soc., Chem. Commun.*, 817 (1978).
(7) A. Hamada and T. Takizawa, *Chem. Pharm. Bull.*, **23**, 2987 (1975).
(8) The integration of the ^{1}H NMR spectrum of the crude reaction mixture demonstrated the presence of **3** and **7** in equimolar amounts. The difference in the isolated yields may be attributed to decomposition of **3** under the separation conditions.

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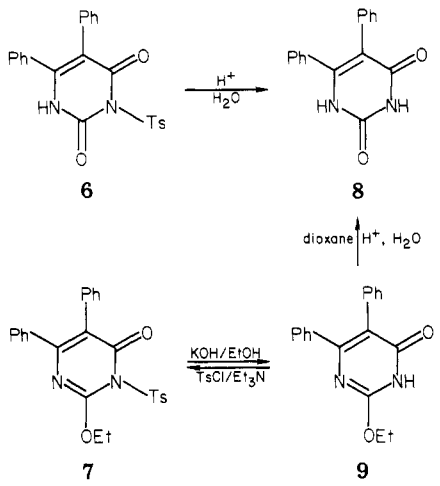


In Scheme I, the formation of **5** is depicted as involving reaction of a second equivalent of **3** on an initially formed ketenimine intermediate (**10**), with migration of a carbethoxy group. The thermal behavior of **5** suggests a reversibility for this process, with possible participation of a thermally unstable iminooxazine (**11**) in the formation of **6** and **7**. Migration of an ylide substituent is, to the best of our knowledge, without precedent in the chemistry of cyclopropenone derivatives, although such a process (involving a six-membered transition state) has been observed[9] in a reaction of ketene dimer.

When a reaction of **2** with **3** in a 1:2 molar proportion was carried out, **5** was now the major product but was still accompanied by an appreciable quantity of **4** (see Table I). This same reaction in the presence of pyridine (2 equiv) reverted the yields to approximately those of a 1:1 situation, thus demonstrating the participation of pyridine in the formation of **4**.[10] We suggest that this participation involves initial substitution in a Michael-addition intermediate (**12**) to yield **13**, followed by rearrangement to the ylide **14** with subsequent migration of the tosyl group and elimination of pyridine. This route may be contrasted with that proposed[7] for the reaction of **2** with triphenylphosphine, where initial nucleophilic attack at sulfur is indicated.

Although reaction of **1** with pyridinium *N*-benzoylamide was observed[3] in benzene under reflux conditions, no reaction of the latter with **2** could be detected even after 10 days under reflux conditions.

(B) Reaction of 2 with Pyridinium Methylides. While no reaction occurred between **2** and pyridinium dicyanomethylide during 7 days in acetonitrile under reflux conditions (contrast with the behavior or **1** cited in the introduction), a smooth reaction was observed with the cyanocarbethoxy analogues **15a–c** (acetonitrile, reflux, 24 h), producing the internal salts **16a–c** in high yield (Scheme II). The presence of a pyridinium nucleus in these products was evident from the appearance of low-field signals (δ 8–8.7) in the ^{1}H NMR spectra. When the reaction of **15a** was carried out in the presence of excess 3,5-lutidine, **16c** was obtained in 68% yield,[11] thus suggesting the participation of a pyridine-free intermediate such as **17a**. Finally, **16a–c** could be smoothly converted, through **18** and **19**, to 2,6-diamino-3,4-diphenylpyridine (**20**). An alternative route to **20** employed ammonolysis of **21** followed by hydrogenolysis of **22** (Scheme III). The picrates of the products obtained from both approaches were identical in all respects. That **19** is, in fact, the 2-toluenesulfonamido isomer was demonstrated by partial hydrolysis of its diacetyl derivative **23** to **24**, whose ^{1}H NMR spectrum showed a one hydrogen singlet at δ 7.80 (C_5 H), a position attributable[12] to a diamagnetic anisotropic effect of the 6-acetamido group. Also, monotosylation of **20** afforded **25** (isomeric with **19**), a product of reaction at the sterically less hindered nitrogen.

The reaction of the dicarbethoxymethylide **15d** and **2** gave a product (**26**, Scheme IV) reminiscent of the product[4] of monosubstituted methylides and **1**. Mild basic hydrolysis of **26** produced the α,β-unsaturated amide **27**, whose ^{1}H NMR spectrum contained two equivalent carbethoxy groups. The monocarbethoxymethylide **15e** and the benzoylmethylide **15f** showed behavior analogous to that of **15d**, affording **28** and **29**, respectively. Acid hydrolysis of **29** produced the known 3,4,6-triphenyl-2-pyrone (**30**).

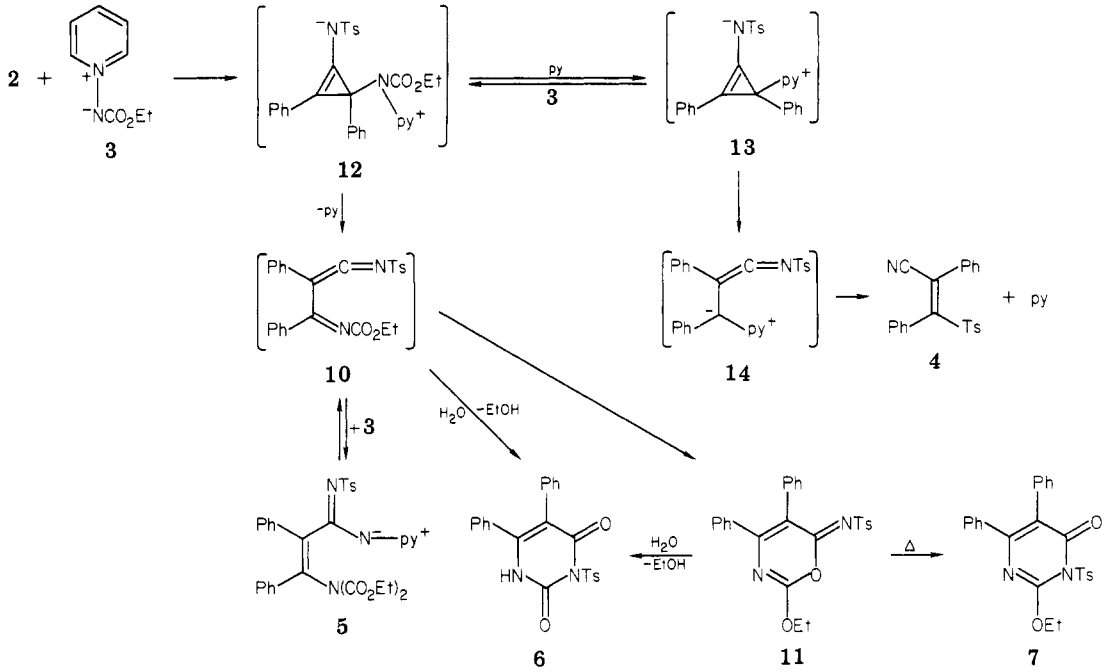
The products obtained from the reactions of **2** with pyridinium ylides may best be accounted for by considering pathways involving participation of ketenimine intermediates (i.e., **10** and **17a,b**; Schemes I, II, and IV). While the ketene counterparts suggested in the reactions of **1** with certain pyridinium ylides show a tendency to undergo cyclization, our results with **2** demonstrate that further reaction with nucleophiles present in the medium may be expected in this case.

(C) Reaction of 2 with Isoquinolinium Ylides. Reaction of the isoquinolinium methylides **31a–c** with **2** paralleled that of the pyridinium analogues, producing **32** (80%), **26** (25%), and **29** (57%), respectively (Scheme V). Acid hydrolysis of **32** afforded α-pyrone **18** (95%).

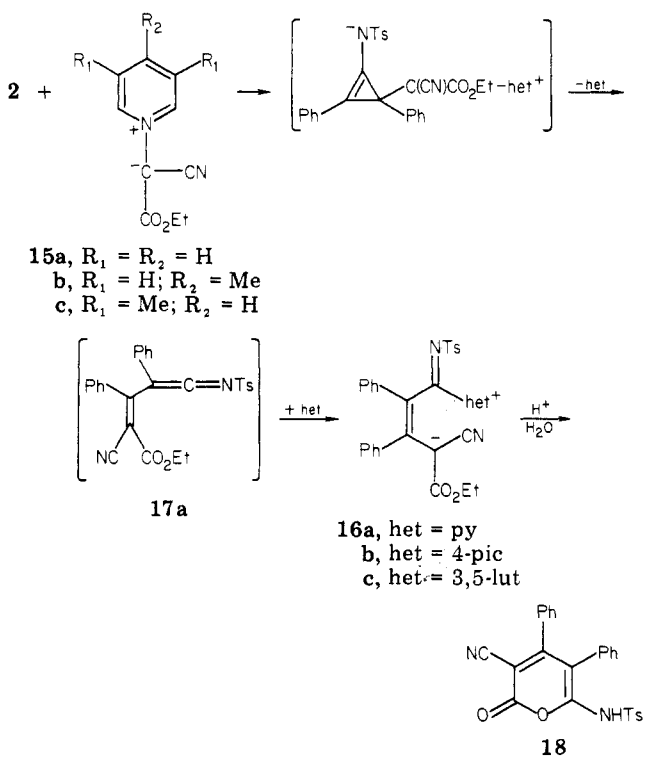
The isoquinolinium *N*-amide derivatives **33a,b**, however, differed markedly in their reactivity toward **2**. With these systems, high yields of cycloadducts **34a,b** were obtained (Scheme VI). These were shown to be 1:1 adducts from ^{1}H NMR and mass spectral analyses. Cleavage of the carbethoxy group in **34a** could be effected in KOH–ethanol under reflux conditions (6 h) to yield **35**, while prolonged heating with base (38 h) afforded 1-benzylisoquinoline (**36**). Benzoylation of **35** produced **34b**. Interestingly, under the conditions in which **34a** gave **36**, **34b** suffered hydrolysis at the 2-position to yield **37**, which was immediately recognized as a potential cycloadduct from **33b** and diphenylcyclopropenone (**1**). Inasmuch as **1** does not undergo cycloadditions with pyridinium *N*-amides,[3] it was considered to be of interest to compare its reactivity with **33b**. In fact, a reaction in benzene under reflux conditions (96 h) afforded **37** (28%) in addition to 2,4,5-triphenyl-1,3-oxazin-6-one (41%), previously isolated[3] as the sole product (80% yield) in the reaction of the corresponding pyridinium *N*-amide. Reaction of **33a** with **1** (benzene, room temperature, 16 h) produced the expected 2-ethoxy-4,5-diphenyl-1,3-oxazin-6-one[3] (55%), and, in addition, **39** (10%), which was found to undergo tautomerism to **40** in KOH–ethanol at room temperature (67 h). Under more vigorous conditions (reflux, 6 h), **39** yielded **40** (17%), an unstable decarboxylation product (16%) which upon

(9) T. Kato, T. Chiba, and S. Tanaka, *J. Heterocycl. Chem.*, **13**, 461 (1976).
(10) Under these same conditions, pyridine did *not* react with **2**.
(11) Neither **2**, **15a**, nor **16a** reacted with 3,5-lutidine under the conditions employed.
(12) N. Enomoto and M. Kondo, *Bull. Chem. Soc. Jpn.*, **45**, 2665 (1972).
(13) A. Balasubramanian, J. M. McIntosh, and V. Snieckus, *J. Org. Chem.*, **35**, 433 (1970).
(14) F. Kröhnke, *Ber. Dtsch. Chem. Ges.*, **68**, 1177 (1935); **70**, 543 (1937); *Ber. Dtsch. Chem. Ges. B*, **72**, 83 (1939).
(15) W. J. Lin, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 3651 (1965).
(16) E. J. Moriconi and Y. Shimakawa, *J. Org. Chem.*, **37**, 196 (1972).
(17) P. I. Mortimer, *Aust. J. Chem.*, **21**, 467 (1968).
(18) A. Kakehi and S. Ito, *Bull. Chem. Soc. Jpn.*, **47**, 938 (1974).

Scheme I



Scheme II



benzoylation afforded **37**, and a decarboxylation–oxidation product assigned structure **41** (37%). It was possible to obtain a mixture of **41** and **42** (33% total) from **33c** and **1** in methanol. The ^{1}H NMR spectrum of the mixture contained one-hydrogen doublets at δ 4.80 and 5.85 (J = 16 Hz, trans-diaxial relationship in **42**) which disappeared upon heating in benzene, with consequent quantitative isolation of **41**. The major product from the reaction of **33c** with **1** proved to be methyl α-phenyl-β-aminocinnamate (60% yield), which had been isolated[19] in high yield as the only product from pyridinium N-amide and **1**. The series of reactions presented in Scheme VI serves to correlate the structures of all compounds obtained from **33a–c**.

To the best of our knowledge cyclopropenimine **2** represents the first case of a system capable of differentiating nucleophilic and dipolar character in a homologous series of cycloiminium methylides and imines. It is of interest to note that ESCA studies on the charge distribution in pyridinium methylides and imines have shown[20] that the former should behave as nucleophiles while the latter should demonstrate 1,3-dipolar behavior. The results of the present study would suggest that the isoquinolinium system may serve as a more efficient probe for such reactivity differences, especially for the cases of other reactive cyclopropene derivatives.

Experimental Section

Melting points were obtained on a Mettler PF 52 melting point apparatus and are uncorrected.

Infrared spectra were recorded with a Perkin-Elmer 337 spectrophotometer.

^{1}H NMR and ^{13}C NMR spectra were recorded with Varian T-60 and XL-100 spectrometers, respectively, with tetramethylsilane as an internal standard.

The mass spectra were recorded with a MAT-311A spectrometer, and the elemental analyses were kindly performed by Rhodia Industrias Quimicas e Texteis S.A.

Materials. The pyridinium N-amides were prepared by Snieckus' method,[13] the pyridinium and isoquinolinium methylides by Kröhnke's method[14] (except pyridinium dicyanomethylide[15] and [3]1c, the latter of which was generated in situ from phenacylisoquinolinium iodide[22]). The isoquinolinium N-amides were prepared by the method described by Huisgen.[23] Diphenylcyclopropenone (**1**) and cyclopropenimine **2** were prepared by Breslow's[21] and Paquette's[2] methods, respectively.

Reactions of Cyclopropenimine 2 with Pyridinium N-Carbethoxyamide (3). (A) Equimolar Mixture in Benzene.

(19) A. Kascheres and D. Marchi, Jr., *J. Org. Chem.*, **40**, 2985 (1975).

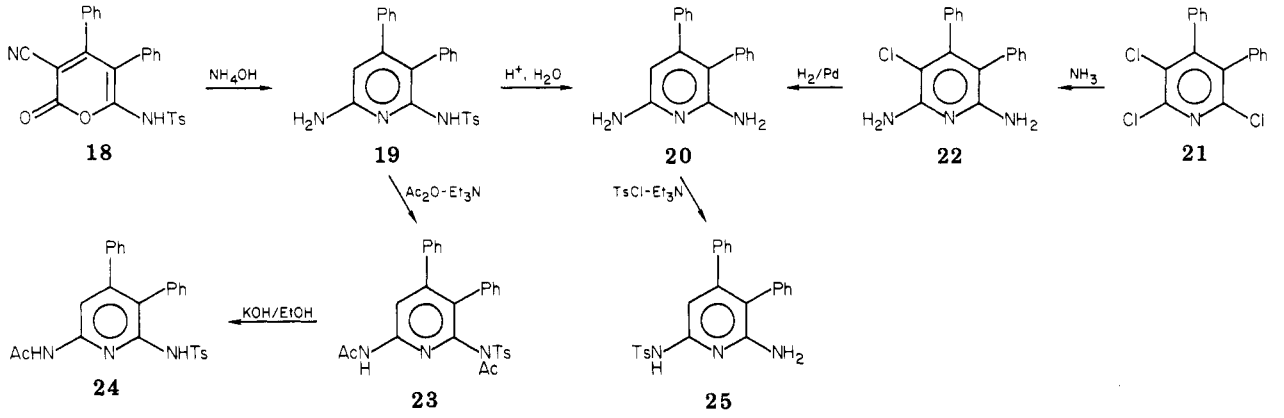
(20) J. P. Catteau, A. Lablache-Combier, J. Grimbolt, M. Nastasi, and J. Streith, *Tetrahedron*, **31**, 2909 (1975).

(21) R. Breslow, R. Hayne, and J. Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959).

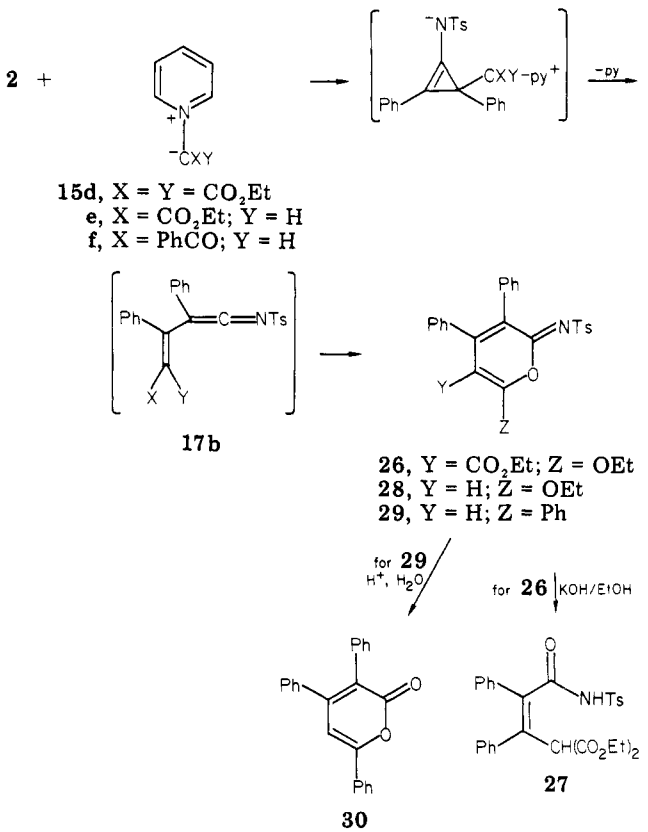
(22) L. C. King and M. McWhirter, *J. Am. Chem. Soc.*, **68**, 717 (1946).

(23) R. Huisgen, R. Grashey, and R. Kriscke, *Justus Liebigs Ann. Chem.*, 506 (1977).

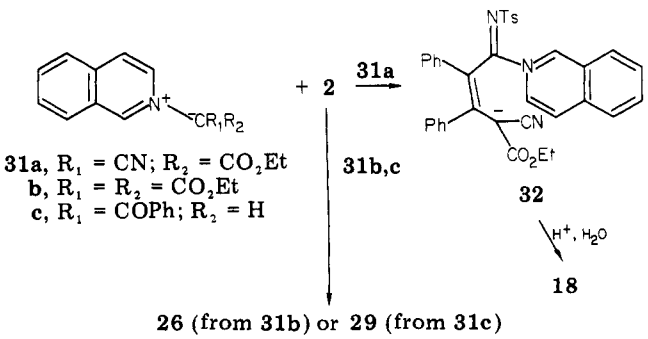
Scheme III



Scheme IV



Scheme V



A solution of cyclopropenimine **2** (0.359 g, 1 mmol) and *N*-carbethoxyamide **3** (0.166 g, 1 mmol) in benzene (10 mL) was refluxed for 6 days. The solvent was removed under reduced pressure, and the residue was separated by column chromatography on silica gel.

Isolation of Pyrimidinone 7. Elution with benzene afforded **7** as a colorless solid (0.022 g, 5%) after recrystallization from CH_2Cl_2–petroleum ether: mp 157.0–157.5 °C; IR (KBr) 1606, 1392, 1367, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 2.47 (s, 3 H, $CH_3C_6H_4SO_2$), 4.39 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 7.0–7.5 (m, 12 H, aromatics), 7.90 (d, 2 H, J = 9.0 Hz, aromatics); MS, m/e 382 ($M^+ \cdot - SO_2$, 9%). Anal. Calcd for $C_{25}H_{22}N_2O_4S$: C, 67.25; H, 4.97; N, 6.27. Found: C, 66.96; H, 4.86; N, 6.15.

Isolation of *trans*-Stilbene 4. Elution with benzene–chloroform (95:5 v/v) afforded after recrystallization from CH_2Cl_2–petroleum ether 1-cyano-2-(*p*-tolylsulfonyl)-*trans*-stilbene (**4**) as a colorless solid: 0.126 g (35%); mp 138.0–139.0 °C (lit.[7] mp 138.5–139.5 °C).

Isolation of the Uracil Derivative 6. Elution with chloroform afforded **6** as a colorless solid (0.054 g, 13%) after recrystallization from CH_2Cl_2–petroleum ether: mp 240.0–240.5 °C; IR (KBr) 3225, 3205, 1735, 1685, 1640, 1396, 1200 cm^{-1}; ^1H NMR [$(CD_3)_2SO$] δ 2.50 (s, 3 H, $CH_3C_6H_4SO_2$), 7.0–7.8 (m, 12 H, aromatics), 8.13 (d, 2 H, J = 9.0 Hz, aromatics), 11.6 (br, 1 H, NH); MS, m/e (relative intensity) 418 ($M^+ \cdot$, 2). Anal. Calcd for $C_{23}H_{18}N_2O_4S$: C, 66.01; H, 4.33; N, 6.69. Found: C, 66.12; H, 4.29; N, 6.62.

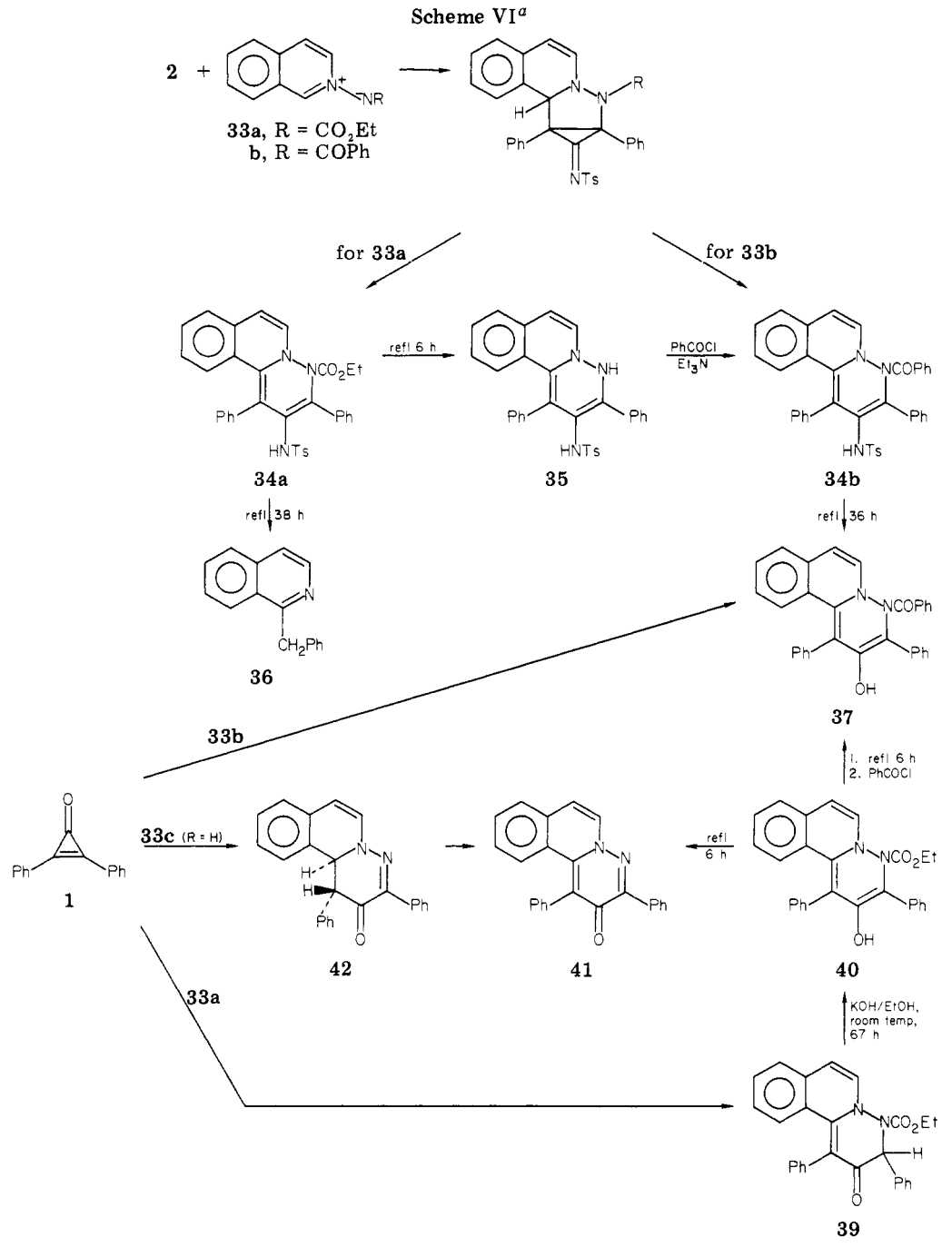
Isolation of Pyridinium *N*-Amide 5. Elution with chloroform–methanol (99:1 v/v) afforded **5** (0.153 g, 25%) as a colorless solid after recrystallization from CH_2Cl_2–petroleum ether: mp 191.5–192.0 °C; IR (KBr) 1785, 1760 (sh), 1710, 1320 (sh), 1300 (sh), 1280, 1140 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 13.82, 21.27, 63.05, 125.39–130.27, 134.50, 135.66, 136.23, 137.01, 140.22, 142.96, 152.81, 164.56; ^1H NMR ($CDCl_3$) δ 1.17 (t, 6 H, J = 7.0 Hz, OCH_2CH_3), 2.28 (s, 3 H, $CH_3C_6H_4SO_2$), 4.20 (q, 4 H, J = 7.0 Hz, OCH_2CH_3), 6.8–7.5 (m, 14 H, β-H's of pyridinium + other aromatics), 7.67 (d, 2 H, J = 8.0 Hz, aromatics), 8.1 (t, 1 H, br, γ-H of pyridinium), 8.27 (dd, 2 H, J = 6.0 and 2.0 Hz, H's α-pyridinium). Anal. Calcd for $C_{33}H_{32}N_4O_6S$: C, 64.69; H, 5.26; N, 9.14; S, 5.23. Found: C, 64.77; H, 5.15; N, 9.06; S, 4.89.

Thermolysis of Pyridinium *N*-Amide 5. A solution of pyridinium *N*-amide **5** (0.122 g, 0.2 mmol) in toluene (5 mL) was refluxed for 4 days. Evaporation of the solvent under reduced pressure and column chromatography on silica gel of the oily residue afforded pyrimidinone **7** (0.037 g, 41%; elution with benzene), uracil derivative **6** (0.023 g, 28%; elution with chloroform), and *N*-carbethoxyamide **3** (0.006 g, 19%;[8] elution with chloroform–methanol, 99:1 v/v).

Basic Hydrolysis of Pyrimidinone 7. The pyrimidinone **7** (0.031 g, 0.07 mmol) was treated at room temperature with ethanolic KOH (10%, 5 mL). After 3 h, the solvent was removed under reduced pressure and the residue diluted with water (20 mL). Acidification with aqueous HCl (37%, pH 4–5) afforded an insoluble solid which was recrystallized from CH_2Cl_2–petroleum ether, yielding pyrimidinone **9**: 0.020 g (97%); mp 240–241 °C; IR (KBr) 3150 (br), 1668 (sh), 1658, 1612 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 4.58 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 7.0–7.4 (m, 11 H, aromatics and NH); MS, m/e (relative intensity) 292 ($M^+ \cdot$, 78).

Tosylation of Pyrimidinone 9. A solution of pyrimidinone **9** (0.006 g, 0.02 mmol) in CH_2Cl_2 (1 mL) was treated with triethylamine (0.1 mL) and excess of *p*-toluenesulfonyl chloride. After 1 h at room temperature, dilution with CH_2Cl_2 (10 mL) and addition of petroleum ether separated ammonium salts. The

Scheme VI[a]



[a] refl = KOH-EtOH, reflux conditions.

residue obtained after evaporation of the solvent afforded pyrimidinone **7** (0.004 g, 45%) by preparative TLC on silica gel with benzene as the eluting solvent.

Acid Hydrolysis of Pyrimidinone 9. A solution of pyrimidinone **9** (0.012 g, 0.04 mmol) in THF (1 mL) was treated with aqueous HCl (37%, 1 mL). After 18 h at room temperature, the solution was diluted with distilled water (8 mL) and neutralized with $NaHCO_3$ (pH 7–8). Extraction with CH_2Cl_2 and recrystallization from CH_2Cl_2–petroleum ether afforded 5,6-diphenyluracil (**8**): 0.010 g (100%); mp 301.0–302.5 °C (lit.[16] mp 302–303 °C). The IR spectrum was superimposible with that of an authentic sample.

Acid Hydrolysis of Uracil Derivative 6. The uracil derivative **6** (0.058 g, 0.14 mmol) was dissolved in H_2SO_4 (97%, 2 mL) with ice-bath cooling; after 16 h at room temperature, the solution was diluted with distilled water (20 mL), and neutralized with K_2CO_3. The insoluble solid was recrystallized from CH_2Cl_2–petroleum ether to afford 5,6-diphenyluracil (**8**): 0.022 g (60%); mp 301.0–302.5 °C (lit.[16] mp 302–303 °C). The IR spectrum was superimposible with that of an authentic sample.

Reactions of Cyclopropenimine 2 with Cyanocarbethoxy Methylides 15a–c. (A) Equimolar Mixture in Acetonitrile. An equimolar mixture of cyclopropenimine **2** (0.5 mmol) and cyanocarbethoxy methylides **15a–c** was refluxed in 15 mL of acetonitrile for 24 h.

Isolation of 16a. Evaporation of the solvent under reduced pressure and trituration with chloroform (10 mL) afforded **16a**: 0.247 g (90%); yellow solid; mp 173.5–174.5 °C; IR (KBr) 2200, 1690, 1640, 1285 (sh), 1275, 1140 cm^{-1}; ^1H NMR (CD_3CN) δ 1.57 (br t, 3 H, J = 7.0 Hz, OCH_2CH_3), 2.37 (s, 3 H, $CH_3C_6H_4SO_2$), 4.53 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 6.8–7.4 (m, 12 H, aromatics), 7.77 (d, 2 H, J = 8.0 Hz, aromatics), 7.8–8.2 (br, 2 H, β-H's of pyridinium), 8.44 (br t, 1 H, J = 6.0 Hz, γ-H of pyridinium), 8.67 (br d, 2 H, J = 6.0 Hz, α-H's of pyridinium). Anal. Calcd for $C_{32}H_{27}N_3O_4S$: C, 69.93; H, 4.95; N, 7.65; S, 5.83. Found: C, 69.69; H, 4.85; N, 7.57; S, 5.60.

Isolation of 16b. The same procedure described above afforded **16b**: 0.254 g (90%); yellow solid; mp 193.0–193.5 °C; IR (KBr) 2196, 1700, 1638, 1290 (sh), 1275, 1140 cm^{-1}; ^1H NMR (CD_3CN) δ 1.52 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 2.38 (s, 3 H,

$CH_3C_6H_4SO_2$), 2.58 (s, 3 H, CH_3 of picolinium), 4.48 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 6.8–7.4 (m, 12 H, aromatics), 7.5–7.9 (m, 4 H, β-H's picolinium + other aromatics), 8.50 (d, 2 H, J = 6.0 Hz, α-H's picolinium). Anal. Calcd for $C_{33}H_{29}N_3O_4S$: C, 70.32; H, 5.19; N, 7.45; S, 5.69. Found: C, 69.98; H, 5.39; N, 7.57; S, 5.53.

Isolation of 16c. Evaporation of the solvent under pressure and trituration with ethyl ether (10 mL) afforded **16c**: 0.271 g (94%); yellow solid; mp 162.5–163.0 °C; IR (KBr) 2190, 1705, 1640, 1300 (sh), 1280, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 2.33 (br s, 9 H, $CH_3C_6H_4SO_2$ and CH_3's of lutidinium), 4.40 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 6.6–7.3 (m, 12 H, aromatics), 7.6–7.9 (m, 3 H, γ-H of lutidinium + other aromatics), 8.43 (s, 2 H, α-H's of lutidinium). Anal. Calcd for $C_{34}H_{31}N_3O_4S$: C, 70.69; H, 5.41; N, 7.27. Found: C, 70.61; H, 5.42; N, 7.55.

(B) Equimolar Mixture in Acetonitrile with an Excess of 3,5-Lutidine. Excess of 3,5-lutidine (0.160 g, 1.5 mmol) was added to a solution of an equimolar mixture of cyclopropenimine **2** (0.144 g, 0.4 mmol) and methylide **15a** (0.076 g) in acetonitrile (4 mL). After 24 h under reflux conditions, evaporation of the solvent at reduced pressure and treatment with ethyl ether (6 × 15 mL) afforded a yellow solid (0.157 g, 68%) with a melting point and IR spectrum identical with those of **16c**.

Control experiments showed no reaction between 3,5-lutidine and cyclopropenimine **2**, methylide **15a**, or internal salt **16a**.

Acid Hydrolysis of 16a–c. In a typical experiment, the internal salts **16a–c** (0.2 mmol) were suspended in THF (4 mL) with magnetic stirring and ice-bath cooling and treated with aqueous $HClO_4$ (35%, 4 mL). The suspension dissolved immediately, and after a few minutes a white solid precipitated. Vacuum filtration afforded **18**: 0.084 g (95%); colorless solid; mp 237.0–237.5 °C; IR (KBr) 3130 (br), 1750, 1180 (sh), 1175 cm^{-1}; ^1H NMR [$(CD_3)_2SO$] δ 2.37 (s, 3 H, $CH_3C_6H_4SO_2$), 6.33 (s, br, 1 H, exchanged with D_2O, NH), 7.0–7.5 (m, 12 H, aromatics), 7.87 (d, 2 H, J = 8.0 Hz, aromatics); MS, m/e (relative intensity) 442 (M^+·, 3). Anal. Calcd for $C_{25}H_{18}N_2O_4S$: C, 67.86; H, 4.10; N, 6.33. Found: C, 68.02; H, 4.07; N, 6.16.

Ammonolysis of 18. The α-pyrone **18** (0.133 g, 0.3 mmol) was treated with aqueous NH_3 (30%, 5 mL) at room temperature. After 3 h a colorless solid precipitated and was recrystallized from $CHCl_3$–n-hexane to afford **19**: 0.093 g (75%); mp 198.0–198.5 °C; IR (KBr) 3480, 3380, 3250, 1625, 1610, 1345, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.47 (s, 3 H, $CH_3C_6H_4SO_2$), 4.0–5.0 (br, 2 H, NH_2), 6.23 (s, 1 H, H-5), 6.7–7.4 (m, 13 H, aromatics and NH), 8.07 (d, 2 H, J = 8.0 Hz, aromatics); MS, m/e (relative intensity) 415 (M^+·, 42).

Acid Hydrolysis of 19. A solution of **19** (0.124 g, 0.3 mmol) in H_2SO_4 (95%, 0.5 mL) was heated to 100–110 °C for 1 h. After the mixture was cooled and distilled water (10 mL) added, an insoluble solid separated and was filtered. It was treated with $NaHCO_3$ solution (5%, 10 mL) and extracted with CH_2Cl_2 (3 × 15 mL), and the organic phase was dried over $MgSO_4$. Evaporation under reduced pressure afforded **20** (0.055 g, 70%) after recrystallization from CH_2Cl_2–n-hexane: mp 125.0–126.5 °C; IR (KBr) 3460, 3360, 3310 (sh), 3180 (br), 1650 (sh), 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.0–4.6 (br, 4 H, 2 NH_2 groups), 6.07 (s, 1 H, H-5), 7.0–7.4 (m, 10 H, aromatics). Picrate (recrystallized from ethanol): mp 220–222 °C; IR (KBr) 3440, 3345, 3170 (br), 1650, 1610 cm^{-1}. Anal. Calcd for $C_{23}H_{18}N_6O_7$: C, 56.33; H, 3.70; N, 17.14. Found: C, 56.60; H, 3.79; N, 16.94.

Alternative Route to 2,6-Diamino-3,4-diphenylpyridine (20). (A) Ammonolysis of 2,5,6-Trichloro-3,4-diphenylpyridine (21). A mixture of **21**[17] (0.200 g, 0.6 mmol), $CuSO_4 \cdot 5H_2O$ (0.200 g, 0.8 mmol), aqueous NH_3 (30%, 8 mL), and ethanol (4 mL) was heated in stainless steel bomb at 190–200 °C during 6 h. After cooling to room temperature, the mixture was poured into distilled water (50 mL). After extraction with ethyl ether (5 × 50 mL), the combined extracts were washed with distilled water (5 × 50 mL), dried over $MgSO_4$, and evaporated under reduced pressure. Purification of the oily residue by alumina chromatography (elution with chloroform) afforded **22** (0.074 g, 42%) as a colorless solid, after recrystallization from CH_2Cl_2–petroleum ether: mp 239.5–241.5 °C; IR (KBr) 3480, 3375, 3350 (br), 1625, 1600 cm^{-1}; MS, (relative intensity) 297 (33), 295 (100), 295.0864 (calcd for $C_{17}H_{14}N_3Cl$, 295.0876).

(B) Hydrogenolysis of 2,6-Diamino-5-chloro-3,4-diphenylpyridine (22). A solution of **22** (0.206 g, 0.7 mmol) in ethanol (50 mL) was submitted to hydrogenolysis (3.0 atm) during 40 h in the presence of 10% Pd/C catalyst (0.80 g) and potassium acetate (40 mmol). After filtration and evaporation under reduced pressure, the oily residue was dissolved in distilled water (30 mL), neutralized with $NaHCO_3$, and extracted with CH_2Cl_2 (5 × 20 mL). From the organic phase 2,6-diamino-3,4-diphenylpyridine (**20**; 0.100 g, 55%) was obtained, whose IR spectrum was superimposible on that of a sample obtained from the acid hydrolysis of **19** above.

Acetylation of 19. Compound **19** (0.062 g, 0.15 mmol) was dissolved in pyridine (1 mL), and, after addition of acetic anhydride (2 drops), the solution was refluxed 1 h. After the mixture cooled to room temperature, distilled water (40 mL) was added with ice-bath cooling, and the insoluble solid was collected by vacuum filtration. Recrystallization from $CHCl_3$–petroleum ether afforded **23**: 0.060 g (80%); colorless solid; mp 233.5–234.0 °C; IR (KBr) 3400, 3285, 3250 (sh), 1720 (sh), 1700, 1370, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.93 (s, 3 H), 2.27 (s, 3 H), 2.40 (s, 3 H), 7.0–7.4 (m, 12 H, aromatics), 7.77 (d, 2 H, J = 8.0 Hz, aromatics), 8.17 (br s, 1 H, exchanged with D_2O, NHAc), 8.05 (s, 1 H, H-5); MS, m/e (relative intensity) 499 (M^+·, 2). Anal. Calcd for $C_{28}H_{25}N_3O_4S$: C, 67.32; H, 5.04; N, 8.41. Found: C, 66.99; H, 4.97; N, 8.27.

Basic Hydrolysis of 23. The diacetyl derivative **23** (0.090 g, 0.18 mmol) was treated (room temperature) with ethanolic KOH (1%, 30 mL) during 62 h. Evaporation under reduced pressure, addition of distilled water (20 mL), and acidification with HCl (37%) until pH 5.0 afforded a colorless insoluble solid. Extraction with CH_2Cl_2 (2 × 15 mL), drying over $MgSO_4$, and evaporation under reduced pressure yielded **24** (72%) as a colorless solid: mp 256.5–257.5 °C; IR (KBr) 3354, 3285, 1700, 1330, 1155 cm^{-1}; ^1H NMR [$(CD_3)_2SO$] δ 2.17 (s, 3 H), 2.38 (s, 3 H), 6.8–7.4 (m, 12 H, aromatics), 7.80 (s, 1 H, H-5), 8.07 (d, 2 H, J = 8.0 Hz, aromatics), 9.18 (br s, 1 H, NH), 10.05 (br s, 1 H, NH); MS, m/e (relative intensity) 457 (M^+·, 3). Anal. Calcd for $C_{26}H_{23}N_3O_3S$: C, 68.25; H, 5.07; N, 9.18. Found: C, 68.47; H, 5.11; N, 9.08.

Monotosylation of 20. To a solution of **20** (0.099 g, 0.4 mmol) in benzene (10 mL) was added p-toluenesulfonyl chloride (0.55 mmol) and triethylamine (0.1 mL). After 18 h at room temperature, the insoluble material was separated by filtration and the filtrate evaporated under reduced pressure. Column chromatography of the oily residue afforded **25** (0.100 g, 60%) by elution with ethyl ether–methanol (19:1, v/v); mp 191.0–192.0 °C; IR (KBr) 3350, 3290, 3180, 1620, 1350, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.47 (s, 3 H, $CH_3C_6H_4SO_2$), 5.87 (br, 2 H, NH_2), 6.97 (s, 1 H, H-3), 7.1–7.6 (m, 13 H, aromatics and NHTs), 7.97 (d, 2 H, J = 8.0 Hz, aromatics); MS, m/e 415.1365 (calcd for $C_{24}H_{21}N_3O_2S$, 415.1354).

Reaction of Cyclopropenimine 2 with Dicarbethoxy Methylide 15d. An equimolar mixture of methylide **15d** (0.261 g, 1.1 mmol) and cyclopropenimine **2** (0.395 g) was dissolved in CH_2Cl_2 (11 mL) and kept at room temperature for 10 days. Addition of petroleum ether afforded, after separation of oily fractions **26** (0.171 g, 30%) as a colorless solid after recrystallization from CH_2Cl_2–petroleum ether: mp 159.0–160.0 °C; IR (KBr) 1730, 1645 (sh), 1635, 1290, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 1.53 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 2.33 (s, 3 H, $CH_3C_6H_4SO_2$), 3.90 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 4.80 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 6.8–7.4 (m, 12 H, aromatics), 7.70 (d, 2 H, J = 8.0 Hz, aromatics); MS, m/e (relative intensity) 517 (M^+·, 2). Anal. Calcd for $C_{28}H_{27}NO_6S$: C, 67.29; H, 5.25; N, 2.71. Found: C, 67.52; H, 5.08; N, 2.68.

Basic Hydrolysis of 26. The treatment of **26** (0.196 g, 0.38 mmol) with ethanolic KOH (10%; 10 mL) for 1 h (room temperature) and evaporation of the solvent afforded an oily residue which was dissolved in distilled water (20 mL). Acidification with HCl (37%) until pH 6.0, extraction with CH_2Cl_2 (3 × 15 mL), and evaporation of the solvent under reduced pressure furnished an oily residue which was triturated with cyclohexane. The α,β-unsaturated amide **27** (0.134 g, 66%) was isolated as a colorless solid: mp 139.0–139.5 °C; IR (KBr) 3270, 1755, 1730, 1715, 1350, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (t, 6 H, J = 7.0 Hz, 2 OCH_2CH_3), 2.48 (s, 3 H, $CH_3C_6H_4SO_2$), 4.00 (q, 4 H, J = 7.0 Hz, 2 OCH_2CH_3), 5.33 (s, 1 H, $CH(CO_2Et)_2$), 6.9–7.5 (m, 13 H, aro-

matics and NHTs), 7.93 (d, 2 H, J = 8.0 Hz, aromatics). Anal. Calcd for $C_{29}H_{29}NO_7S$: C, 65.03; H, 5.45; N, 2.61. Found: C, 65.33; H, 5.54; N, 2.55.

Reaction of Cyclopropenimine 2 and Monocarbethoxy Methylide 15e. A solution of cyclopropenimine **2** (0.215 g, 0.6 mmol) and monocarbethoxy methylide **15e** (0.165 g, 1.0 mmol), generated in situ by addition of triethylamine to a suspension of the corresponding pyridinium salt,[18] in CH_2Cl_2 (10 mL) was kept at room temperature for 48 h. The solvent was removed under reduced pressure, and column chromatography on silica gel (elution with benzene–ethyl ether, 9:1 v/v) and recrystallization from CCl_4–n-hexane furnished **28**: 0.059 g (22%); yellow solid; mp 58.0–59.5 °C; IR (KBr) 1645, 1295, 1150 cm^{-1}; ^1H NMR (CCl_4) δ 1.60 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 2.40 (s, 3 H, $CH_3C_6H_4SO_2$), 4.80 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 5.78 (s, 1 H, H-5), 6.9–7.3 (m, 12 H, aromatics), 7.83 (d, 2 H, J = 8.0 Hz, aromatics); MS, m/e (relative intensity) 445 ($M^{+\cdot}$, 1.4), 445.1373 (calcd for $C_{26}H_{23}NO_4S$, 445.1348).

Reaction of Cyclopropenimine 2 and the Benzoylmethylide 15f. A solution of cyclopropenimine **2** (0.108 g, 0.3 mmol) and benzoylmethylide **15f** (0.079 g, 0.4 mmol), generated in situ by addition of triethylamine to a suspension of the corresponding salt,[14] was kept at room temperature for 48 h. The solvent was removed under reduced pressure, and after crystallization of the ethyl ether insoluble fraction with CH_2Cl_2–petroleum ether, **29** was obtained: 0.086 g (60%); mp 207.0–208.0 °C; IR (KBr) 1641, 1295, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (s, 3 H), 6.90 (s, 1 H), 7.0–8.2 (m, 19 H); MS, m/e (relative intensity) 477 (2). Anal. Calcd for $C_{30}H_{23}NO_3S$: C, 75.45; H, 4.85; N, 2.92. Found: C, 75.24; H, 4.67; N, 2.95.

Acid Hydrolysis of 29. To a solution of **29** (0.057 g, 0.12 mmol) in dioxane (3 mL) was added aqueous HCl (10%, 3 mL) and the suspension was refluxed for 24 h. After the mixture cooled to room temperature, a yellow solid separated (0.039 g, 100%) which was identical (melting point and IR spectrum) with the known[4] 3,4,6-triphenyl-2-pyrone (**30**). Neutralization of the aqueous phase with $NaHCO_3$ and extraction with CH_2Cl_2 afforded p-toluenesulfonamide (0.020 g, 100%) identical (melting point and IR spectrum) with an authentic sample.

Reactions of Cyclopropenimine 2 with Isoquinolinium Methylides 31a–c. Reaction with Isoquinolinium Cyanocarbethoxymethylide 31a. An equimolar solution of cyclopropenimine **2** (0.287 g, 0.8 mmol) and cyanocarbethoxymethylide **31a** (0.192 g) in acetonitrile (8 mL) was refluxed for 24 h.

After solvent evaporation under reduced pressure, the oily residue was treated with ethyl ether, and the insoluble solid was recrystallized from CH_2Cl_2–ethyl ether to yield **32**: 0.383 g (80%); mp 185.0–185.5 °C; IR (KBr) 2195, 1710, 1660, 1270, 1145 cm^{-1}; ^1H NMR (CD_3CN) δ 1.67 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 2.40 (s, 3 H, $CH_3C_6H_4SO_2$), 4.77 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 6.8–7.5 (m, 12 H, aromatics), 7.90 (d, 2 H, J = 8.0 Hz, aromatics), 8.0–8.6 (m, 6 H, isoquinolinium less H-1), 9.75 (s, 1 H, H-1 of isoquinolinium).

Acid Hydrolysis of 32. The internal salt **32** (0.120 g, 0.2 mmol) was suspended in THF (4 mL) with magnetic stirring and ice bath cooling and was treated with aqueous $HClO_4$ (35%, 4 mL). The suspension dissolved immediately, and after a few minutes a colorless solid precipitated. Vacuum filtration afforded **18** (0.084 g, 95%) as a colorless solid (melting point and IR spectrum identical with those of a sample obtained from the acid hydrolysis of **16a–c** as described above).

Reaction with Isoquinolinium Methylide 31b. An equimolar mixture of methylide **31b** (0.287 g, 1.0 mmol) and cyclopropenimine **2** (0.359 g) was dissolved in CH_2Cl_2 (10 mL) and kept at room temperature for 10 days. Addition of petroleum ether afforded **26** (0.129 g, 25%), after separation of oily fractions, with a melting point and IR spectrum identical with those of a sample obtained from the reaction of **15d** as described above.

Reaction with Isoquinolinium Methylide 31c. A solution of cyclopropenimine **2** (0.215 g, 0.6 mmol) and benzoylmethylide **31c** (0.160 g, 0.65 mmol), generated in situ by addition of triethylamine to a suspension of the corresponding salt **12** in CH_2Cl_2 (6 mL), was kept at room temperature for 64 h. The solvent was removed under reduced pressure, and after crystallization of the ethyl ether insoluble fraction with CH_2Cl_2–petroleum ether, **29** (0.163 g, 57%) was obtained (melting point and IR spectrum identical with those of a sample obtained from the reaction of **15f** as described above).

Reactions of Cyclopropenimine 2 with Isoquinolinium *N*-Amides 33a and 33b. Reaction with 33a. An equimolar mixture of cyclopropenimine **2** (0.323 g, 0.9 mmol) and isoquinolinium *N*-amide **33a** (0.194 g) was dissolved in benzene (9 mL) and refluxed for 24 h. The solvent was removed under reduced pressure, and after filtration on silica gel (elution with benzene–ethyl ether, 9:1 v/v) **34a** (0.492 g, 95%) was obtained as a red-orange solid: mp 117.0–118.0 °C; IR (KBr) 3270, 1745, 1630, 1130, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 2.33 (s, 3 H, $CH_3C_6H_4SO_2$), 4.10 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 6.80 (d, 1 H, J = 8.0 Hz, H-6), 7.12 (d, 3 H, J = 9.0 Hz; with D_2O this becomes d, 2 H, J = 9.0 Hz, aromatics and NH), 7.2–7.7 (m, 16 H, aromatics), 7.75 (d, 1 H, J = 8.0 Hz, H-5); MS, m/e (relative intensity) 575 (M^+, 76). Anal. Calcd for $C_{34}H_{29}N_3O_4S$: C, 70.94; H, 5.08; N, 7.30. Found: C, 71.29; H, 5.28; N, 6.97.

Basic Hydrolysis of the Cycloadduct 34a. (a) Reflux during 38 h. A solution of **34a** (0.402 g, 0.7 mmol) in ethanolic KOH (10%, 20 mL) was refluxed during 38 h. After evaporation under reduced pressure and addition of distilled water (80 mL), the suspension was extracted with CH_2Cl_2 (4 × 25 mL). Fractional crystallization from CH_2Cl_2–petroleum ether afforded p-toluenesulfonamide (0.084 g, 70%; melting point and IR spectrum identical with those of an authentic sample), and chromatography on silica gel of the soluble fraction (benzene elution) furnished 1-benzylisoquinoline (**36**): 0.069 g (45%); IR and ^1H NMR spectra and the melting point of the corresponding picrate were identical with those of an authentic sample.[24]

(b) Reflux during 6 h. A solution of **34a** (0.144, 0.25 mmol) in ethanolic KOH (10%, 10 mL) was refluxed during 6 h. After evaporation under reduced pressure and addition of distilled water (60 mL) the insoluble orange solid was separated by vacuum filtration and recrystallized from CH_2Cl_2–petroleum ether to yield **35**: 0.075 g (60%); orange solid; mp 245.0–246.5 °C; IR (KBr) 3343, 3254, 1637, 1135, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (s, 3 H, $CH_3C_6H_4SO_2$), 6.72 (d, 1 H, J = 8.0 Hz, H-6), 7.03 (d, 3 H, J = 9.0 Hz; with D_2O this becomes d, 2 H, J = 9.0 Hz, aromatics and NH), 7.2–8.0 (m, 18 H; with D_2O this becomes m, 17 H, aromatics, NH and H-5); MS, m/e (relative intensity) (M^+, 36). Anal. Calcd for $C_{31}H_{25}N_3O_2S$: C, 73.93; H, 5.00; N, 8.34. Found: C, 74.09; H, 5.28; N, 8.11.

Benzoylation of 35. To a solution of **35** (0.045 g, 0.09 mmol) in benzene (5 mL) were added triethylamine (2 drops) and benzoyl chloride (2 drops). The solution was refluxed during 2 h, and it was diluted with benzene (15 mL) and cooled to room temperature. The insoluble salt was filtered, and evaporation of the organic phase furnished an oily residue which was filtered through silica gel (elution with benzene–ethyl ether, 19:1 v/v) to afford **35b** (0.055 g) as a red solid in quantitative yield: mp 120.5–122.0 °C; IR (KBr) 3400 (br), 1685, 1630, 1130, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (s, 3 H, $CH_3C_6H_4SO_2$), 6.79 (d, 1 H, J = 8.0 Hz, H-6), 6.99 (d, 2 H, J = 9.0 Hz, aromatics), 7.2–7.8 (m, 19 H, aromatics), 7.7–8.1 (m, 3 H, aromatics, H-5), 8.52 (s, 1 H, exchanges with D_2O, NH); MS, m/e (relative intensity) 607 (M^+, 47). Anal. Calcd for $C_{38}H_{29}N_3O_3S$: C, 75.10; H, 4.81; N, 6.91. Found: C, 74.89; H, 4.69; N, 6.82.

Basic Hydrolysis of 34b. A solution of **34b** (0.121 g, 0.20 mmol) in ethanolic KOH (10%, 10 mL) was refluxed during 36 h. After evaporation of the solvent under reduced pressure and addition of distilled water (20 mL) the insoluble yellow solid was separated by vacuum filtration and recrystallized from CH_2Cl_2–petroleum ether to yield **37**: 0.045 g (50%); yellow solid; mp 253.0–254.0 °C; IR (KBr) 3250 (br), 1662, 1631 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.57 (d, 1 H, J = 8.0 Hz, H-6), 7.0–7.6 (m, 16 H, aromatics), 7.6–8.0 (m, 5 H, aromatics, H-5, and OH); MS, m/e (relative intensity) 454 (M^+, 95). Anal. Calcd for $C_{31}H_{22}N_2O_2$: C, 81.92; H, 4.88; N, 6.16. Found: C, 81.68; H, 4.63; N, 6.24.

Neutralization of the aqueous phase with HCl (37%) furnished an insoluble solid which was filtered and recrystallized from CH_2Cl_2–petroleum ether to yield p-toluenesulfonamide in quantitative yield and identical with an authentic sample.

(24) J. R. Keershaw and B. C. Uff, *J. Chem. Soc., Chem. Commun.*, 331 (1966).

Reaction with 33b. An equimolar mixture of cyclopropenimine **2** (0.233 g, 0.65 mmol) and isoquinolinium *N*-amide **33b** (0.161 g) was dissolved in benzene (6.5 mL) and left under reflux conditions during 10 days. The solvent was removed under reduced pressure, and the red solid obtained was recrystallized from CH_2Cl_2–petroleum ether to yield **34b** (0.387 g, 98%), whose IR spectrum was identical with that of a sample obtained from the benzoylation of **35** as described above.

Reactions of Diphenylcyclopropenone (1) with Isoquinolinium *N*-Amides 33a–c. Reaction of 33a. A mixture of **1** (0.577 g, 2.8 mmol) and isoquinolinium *N*-amide **33a** (0.734 g, 3.4 mmol) was dissolved in benzene (170 mL) and kept at room temperature for 16 h. The solvent was removed under reduced pressure, and the oily residue was submitted to chromatography on silica gel, furnishing 2-ethoxy-4,5-diphenyl-1,3-oxazin-6-one (0.448 g, 55% yield from **1**; benzene elution, identical with an authentic sample[3]) and cycloadduct **39** (0.118 g, 10% yield from **1**) as a yellow solid after recrystallization from cyclohexane: mp 168.5–170.0 °C; IR (KBr) 1743, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 4.39 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 5.92 (s, 1 H, H-3), 6.38 (d, 1 H, J = 8.0 Hz, H-6), 6.8–8.2 (m, 15 H, aromatics and H-5); MS, m/e (relative intensity) 422 (M^+, 58). Anal. Calcd for $C_{27}H_{22}N_2O_3$: C, 76.76; H, 5.25; N, 6.63. Found: C, 76.52; H, 5.25; N, 6.34.

Tautomerization of 39. The cycloadduct **39** (0.084 g, 0.2 mmol) was dissolved in ethanolic KOH (10%, 8 mL) and kept at room temperature for 67 h. Evaporation of the solvent under reduced pressure, addition of distilled water (30 mL), neutralization with HCl (37%), and extraction with CH_2Cl_2 afforded an oily residue. Filtration on silica gel with benzene–ethyl ether (4:1, v/v) as eluent afforded **40**: 0.036 g (43%); yellow solid; mp 114.5–116.0 °C; IR (KBr) 3250 (br), 1730, 1660, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 4.16 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 6.10 (br s, 1 H, exchanges with D_2O, OH), 6.62 (d, 1 H, J = 7.0 Hz, H-6), 7.2–8.0 (m, 15 H, H-5 and aromatics); MS m/e (relative intensity) 422 (M^+, 100), 422.1613 (calcd for $C_{27}H_{22}N_2O_3$, 422.1630).

Basic Hydrolysis of 39. A solution of **39** (0.169 g, 0.4 mmol) in ethanolic KOH (10%, 10 mL) was refluxed during 6 h. After solvent evaporation under reduced pressure, addition of distilled water (40 mL), and neutralization with HCl (37%), the resulting solid was treated with ethyl ether, and **41** (0.051 g, 37%) was isolated as an insoluble colorless solid: mp 270.0–271.0 °C; IR (KBr) 1665, 1587, 1582, 1350 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.97 (d, 1 H, J = 8.0 Hz, H-6), 7.2–7.8 (m, 12 H, aromatics), 8.07 (d, 1 H, J = 8.0 Hz, H-5), 8.37–8.60 (m, 2 H, aromatics); MS, m/e (relative intensity) 348 (M^+, 100). Anal. Calcd for $C_{24}H_{16}N_2O$: C, 82.74; H, 4.63; N, 8.04. Found: C, 82.60; H, 4.85; N, 8.00.

The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), and the extracts were combined with the ethyl ether soluble fraction. After solvent evaporation, the oily residue was submitted to chromatography on silica gel. Elution with benzene–ethyl ether (9:1 v/v) afforded **40** (0.029 g, 17%), and elution with benzene–ethyl ether (1:1 v/v) afforded a yellow oil which was treated with benzoyl chloride (2 drops) and triethylamine (1 drop) in benzene (5 mL) at room temperature. After chromatography on silica gel (elution with benzene–ethyl ether (9:1 v/v), **37** (0.029 g, 16%) was isolated as a yellow solid (melting point and IR spectrum identical with those of a sample obtained from the basic hydrolysis of **34b** as described above).

Reaction with 33b. A mixture of **1** (0.185 g, 0.9 mmol) and isoquinolinium *N*-amide **33b** (0.273 g, 1.1 mmol) was dissolved in benzene (54 mL) and left under reflux conditions during 3 days. The solvent was removed under reduced pressure, and the oily residue afforded (after chromatography on silica gel) 2,4,5-triphenyl-1,3-oxazin-6-one (0.120 g, 41% yield from **1**; benzene elution) identical (melting point and IR spectrum) with an authentic sample[3] and **37** [0.114 g, 28% yield from **1**; elution with benzene–chloroform (1:1 v/v)] as a yellow solid.

Reaction with 33c. A solution of **1** (0.144 g, 0.7 mmol) and isoquinolinium *N*-amide **33c** (0.202 g, 1.4 mmol), generated in situ by addition of triethylamine to a suspension of the corresponding salt[23] in methanol (40 mL), was kept at room temperature during 3 h. An insoluble solid was obtained which was a mixture of the cycloadduct **42** and its oxidation product **41** (33% total yield from **1**) in a 1:2 molar ratio. Two doublets in the ^1H NMR spectrum (δ 4.30 and 5.85, J = 16.0 Hz in $CDCl_3$) disappeared when the mixture was left under reflux conditions in benzene (10 mL) during 72 h. After this time, **41** (0.080 g, 33% yield from **1**) was obtained as a colorless solid after recrystallization from CH_2Cl_2–petroleum ether (melting point and IR spectrum identical with those of a sample obtained from the basic hydrolysis of **39** as described above).

Methyl α-phenyl-β-aminocinnamate (0.106 g, 60%) was isolated from the methanol-soluble fraction by means of fractional crystallization from cyclohexane (melting point and IR spectrum identical with those of an authentic sample[19]).

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