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Alkylation of Pyridine 1-Oxides and Related Compounds with Activated Acetylenes. A Novel Molecular Rearrangement of Heteroaromatic *N*-Oxides[1]

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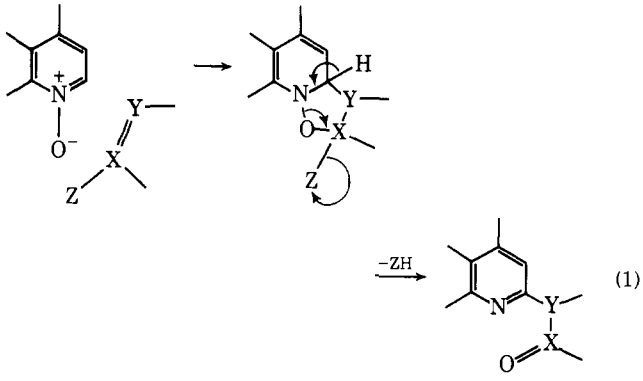
Abstract: The reaction of pyridine 1-oxide with phenylcyanoacetylene gives the 3-alkylated derivative **5** as the main product together with minor amounts of the 2-alkylated product **3**, the ylide **4**, and the divinyl ether **6**. With substituted pyridine 1-oxides and with quinoline 1-oxide the products of 3-alkylation are also formed unless the 3 and 5 positions are blocked. Isoquinoline 1-oxide gives only the corresponding ylide **18**. The structures of the products were confirmed by spectroscopic methods and by the synthesis of authentic samples. Reaction of α-cyanophenacylphenyliodonium ylide with pyridines, quinoline, and isoquinoline gives the *N*-ylides only, but decomposition of benzoylcyanodiazomethane in pyridine gives both the ylide **4** (main product) and **5** via benzoylcyanocarbene. The mechanism of formation of the products is discussed and it is felt that the 3-alkylated products arise from the initial 1,2-dihydro adduct **27** by a $[{}_{\sigma}2_s + {}_{\pi}2_a + {}_{\pi}4_s]$ rearrangement to **29**, followed by regiospecific cyclopropane ring opening to derivatives of **5**.

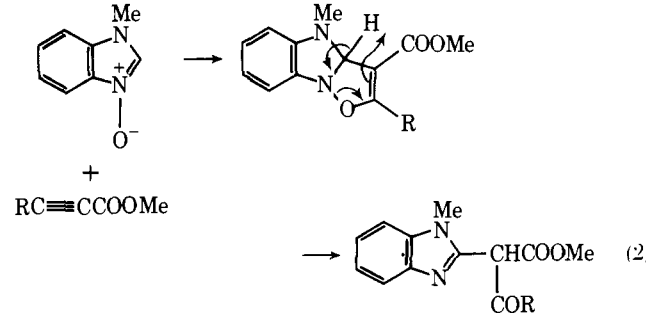
The direct α acylamination of heteroaromatic *N*-oxides using imidoyl chlorides or nitrilium salts[2] probably involves nucleophilic addition of the oxide group to the imidoyl carbon, followed by (or in the case of nitrilium salts perhaps concerted with) intramolecular nucleophilic attack of the nitrogen upon the α position of the pyridine ring, and then aromatization. A related reaction is that of *N*-oxides with isocyanates[3] and the reaction of pyridine 1-oxide with perfluoropropene to give 2-(1,2,2,2-tetrafluoroethyl)pyridine and carbonyl fluoride.[4]

This led us to consider the possibility of a general reaction, as shown in eq 1. In principle, Z could be either a good anionic leaving group or another π bond to Y. The present paper describes an example of the latter situation in which the reactions of some six-membered heteroaromatic *N*-oxides were treated with phenylcyanoacetylene (**1**).



(1)

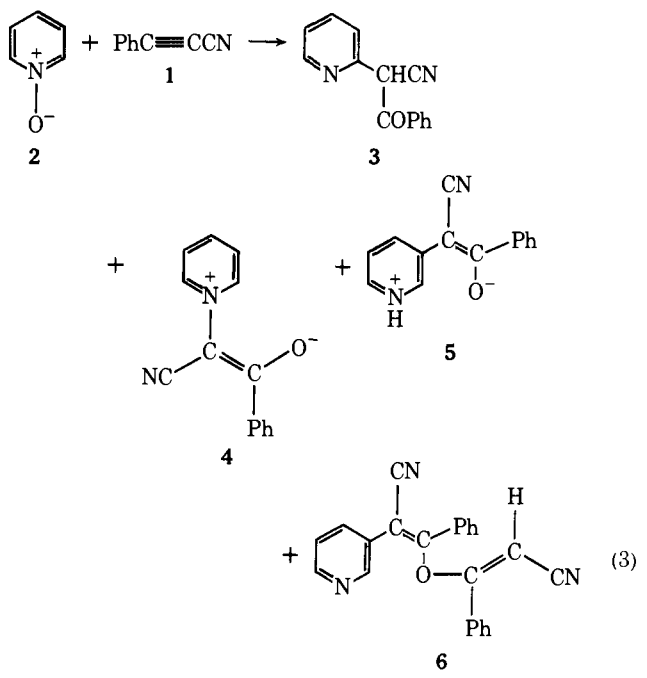
Nitrones undergo 1,3-dipolar cycloaddition with suitable acetylenes[5] and this reaction has been applied successfully to imidazole 3-oxides (eq 2).[6]



(2)

Results

The reaction of pyridine 1-oxide (**2**) with **1** gave three 1:1 adducts and one 1:2 adduct (eq 3). One of the 1:1 adducts, α-cyanophenacylpyridinium ylide (**4**), was a very minor (0.4%) product at best. Its spectral properties were consistent with the



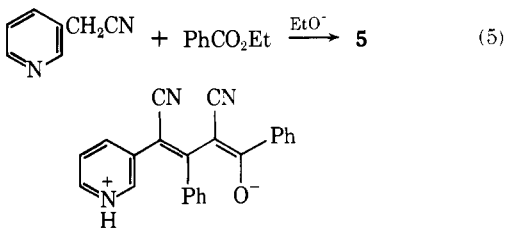
(3)

proposed structure and it was identical with an authentic sample prepared from α-cyanomethylpyridinium chloride[7] and benzoyl chloride to give α-cyanophenacylpyridinium benzoate, then to the perchlorate,[8] and finally treatment with base (eq. 4).[9]

$$[C_5H_5N^+CH_2CN]Cl^- \rightarrow [C_5H_5N^+CH(CN)COPh]PhCO_2^- \rightarrow [C_5H_5N^+CH(CN)COPh]ClO_4^- \xrightarrow{Et_3N} \mathbf{4} \quad (4)$$

The second minor (2.5%) 1:1 adduct was shown to be the expected α-acylalkylation product, 2-α-cyanophenacylpyridine (**3**) on the basis of its spectral properties and its synthesis (in extremely low yield) from pyridine 1-oxide, acetic anhydride, and benzoylacetonitrile.[10]

The major (60.8%) product of the reaction exhibited bands at 2600–2340 ($>NH^+$), 2190 (C≡N), and 2120 cm^{-1} (w, br), and only a very weak broad band at 1640 cm^{-1}, where a highly conjugated carbonyl group might have absorbed. Its NMR spectrum in CF_3CO_2H indicated the presence of two pyridine α protons [δ 9.53 (br s, 1 H, H_2), 8.73 (d, $J_{5,6}$ = 6.0 Hz, H_6)], a pyridine β proton [δ 8.17 (dd, $J_{4,5}$ = 8.9, $J_{5,6}$ = 6.0 Hz, H_5)], and a γ proton [δ 9.04 (d, 1 H, $J_{4,5}$ = 8.9 Hz, H_4)], in addition to the phenyl protons and one proton which underwent H–D exchange with D_2O. These data are consistent with this isomer being a 3-substituted pyridine derivative **5**, and this was confirmed by its hydrolysis with dilute hydrochloric acid to 3-pyridylacetic acid and benzoic acid. This unexpected orientation of the acylalkylation product was confirmed by single-crystal x-ray analysis[1a] of **5** which, in addition, established the *Z* relationship of the phenyl and nitrile groups. An unambiguous synthesis of **5** from 3-pyridylacetonitrile and ethyl benzoate with sodium ethoxide gave a product identical with the product from **1** and **2** (eq 5).

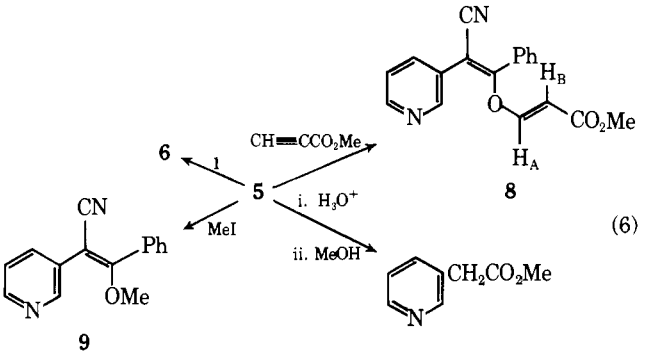


(5)

Table I. Reaction of Picoline and Lutidine 1-Oxides with Phenylcyanoacetylene

Pyridine 1-oxide	Product	% yield
2-Me	**12**	43.4
3-Me	**10** (R = 5-Me)	31.3
4-Me	**10** (R = 4-Me)	27.7
3,5-Me_2	**11**	77.2
3,4-Me_2	**10** (R = 4,5-Me_2)	4.0
2,6-Me_2	**10** (R = 2,6-Me_2)	3.0

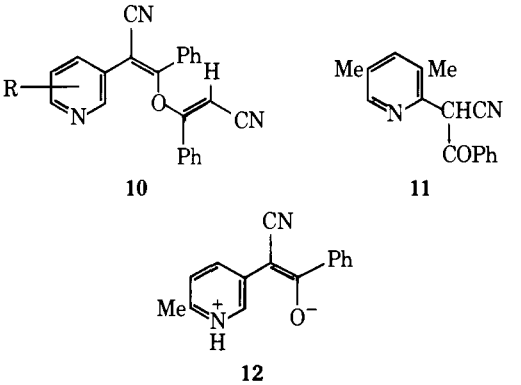
The structure of the 1:2 adduct was initially thought to be **7**.[1a] A more careful study of its NMR spectrum in CF_3CO_2H revealed the presence of a vinylic proton at δ 6.70, inconsistent with structure **7**, but in agreement with this being 1,1′-diphenyl-2,2′-dicyano-2-(3-pyridyl)divinyl ether (**6**). This was confirmed in a number of ways (eq 6). Hydrolysis of **6** gave **5**



(6)

and benzoylacetonitrile. Reaction of **5** with **1** gave a 93% yield of **6**, while reaction with methyl propiolate gave the divinyl ether **8**. The latter has an *E*-acrylate configuration, as indicated by the vinylic coupling constant J_{AB} = 14.0 Hz, and it is on this basis that both phenyls and nitriles are assigned the *Z* configuration in **6**. Methylation of **5** with methyl iodide gave the *O*-methyl ether (**9**) (rather than *C* alkylation, as indicated by the absence of a carbonyl band in the infrared spectrum of the product), which is consistent with the above formation of divinyl ethers.

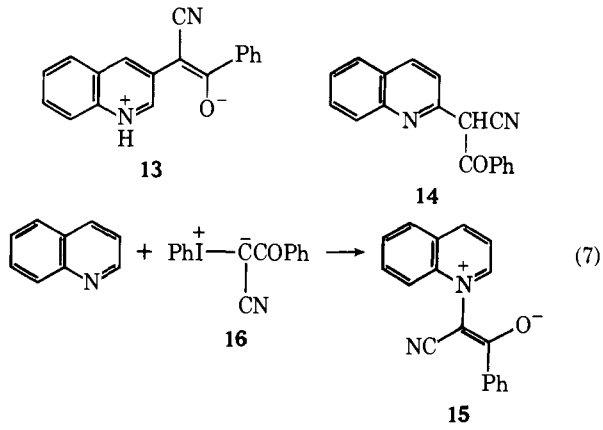
The reaction was extended to the picoline and lutidine 1-oxides with the results summarized in Table I. In most cases, the divinyl ether **10** was the main product (though the yield was rather low), and only in the case of 3,5-lutidine 1-oxide was a good yield of the 2-alkylation product **11** obtained. With 2-



picoline 1-oxide only the 5-acylalkylation product **12** was obtained, none of the 3 isomer being detected (see discussion of the mechanism below). No effort was made in the other cases to isolate any minor products.

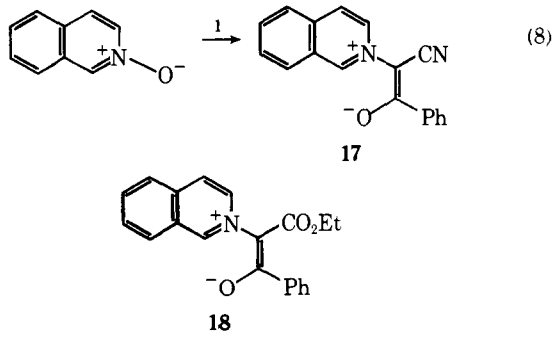
Quinoline 1-oxide and **1** gave the two 1:1 adducts, **13** (25.7%) and **14** (11.3%), in addition to the ylide **15** (8%). The structures of **13, 14,** and **15** were deduced on the basis of their

spectral properties and, in the case of **14,** was confirmed by an unambiguous synthesis from quinoline 1-oxide, acetic anhydride, and benzoylacetonitrile.[10] Reaction of quinoline with α-cyanophenacylphenyliodonium ylide (**16**) (from benzoylacetonitrile, iodosobenzene diacetate, and base) gave a 20% yield of authentic **15** (eq 7). 2-Methylquinoline 1-oxide gave



(7)

only tars with **1.** Isoquinoline 2-oxide, on the other hand, reacted with phenylcyanoacetylene to give mostly the ylide **17** (63%) together with a very low yield of a second isomer (<2%) which has not been characterized (eq 8). An authentic sample

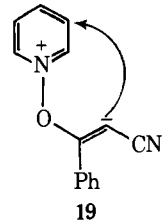


(8)

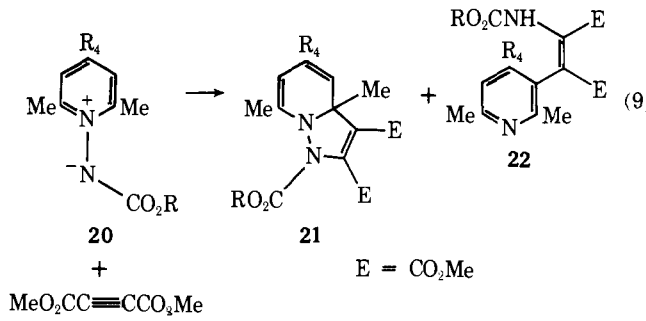
of the ylide (**17**) was obtained in excellent yield from isoquinoline and **16.** Huisgen, Seidl, and Wulff[11] similarly reported the formation of the ylide **18** from isoquinoline 2-oxide and ethyl phenylpropiolate, but no product of *C* alkylation, and they established the structure of **18** by unambiguous synthesis from isoquinoline and ethyl α-bromobenzoylacetate. Analogous ylides have been obtained from 2-methylbenzimidazole 3-oxides,[12] phenanthridine *N*-oxide,[13] and benzocinnoline *N*-oxides.[14]

Discussion

Any proposed mechanism must explain the formation of both 2- and 3-alkylated products as well as that of the ylides. A direct intramolecular attack (**19**) is both sterically and



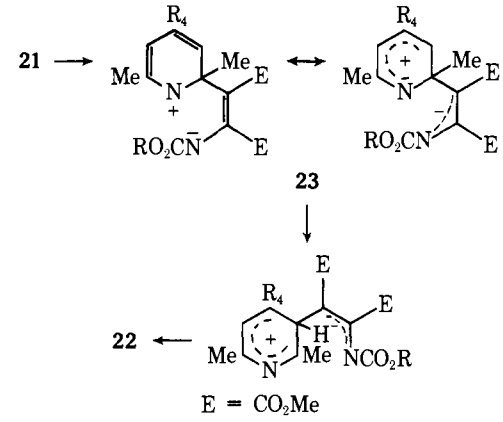
mechanistically unlikely and is not considered further. Sasaki and his co-workers[15] carried out the reaction of 2-methyl- and 2,6-dimethyl-1-alkoxycarbonyliminopyridinium ylides (**20**) with dimethyl acetylenedicarboxylate and isolated both the unstable 1,2-dihydropyridine cycloadducts (**21**) and the 3-alkylated products (**22**) (eq 9). Reaction at a methyl-bearing



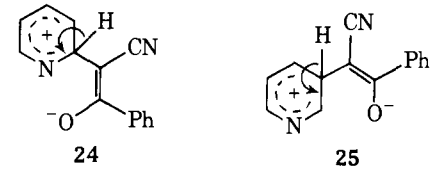
(9)

carbon is in contrast to the above reactions of pyridine 1-oxides, e.g., 2-methylquinoline 1-oxide. They proposed that the initial adduct **21** underwent N–N bond fission to give the zwitterion **23,** which could undergo either a 1,4 shift of the C(2)-vinyl group (presumably ${}_{\sigma}2_a + {}_{\pi}2_a + {}_{\omega}0_a$) or 1,2 shift to give a 5- or 3-substituted zwitterion, which would then aromatize by a 1,4 shift of the β hydrogen (Scheme I). This scheme can be applied

Scheme I



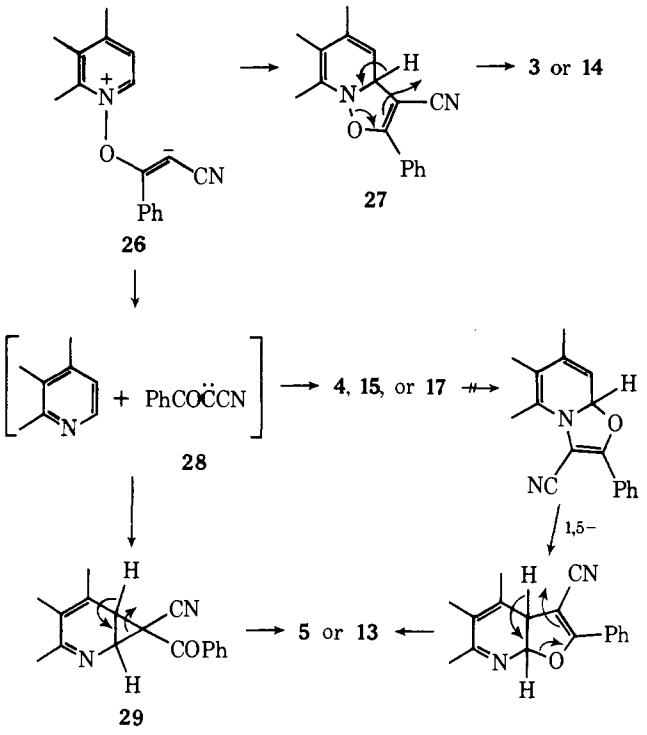
to pyridine 1-oxides but two objections arise. First, the heterolytic N–O bond cleavage leads initially to a nitrenium ion, albeit a resonance stabilized one. Counterbalancing somewhat this energetically unfavorable process is the delocalization of the negative charge in the side chain. More important, perhaps, is that the zwitterion **24** could itself aromatize by losing a proton to give **3** but, instead, would have to prefer to undergo a 1,2- or 1,4-alkyl shift to **25** before then losing a proton to give



5, and it is difficult to see why loss of a proton from the pyridine β position would be more facile than its loss from the α position. This mechanism also fails to account for ylide formation in the *N*-oxide case.

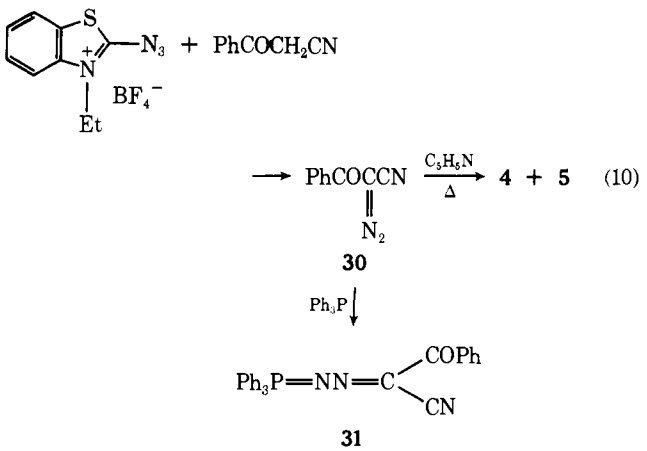
A tentative mechanism was proposed[1a] to account for the formation of all three products (Scheme II). The first step would involve stepwise nucleophilic addition of the *N*-oxide to the acetylene to give **26,** which could ring close to **27** and aromatize to give the α-acylalkylated product. Alternatively, **26** could dissociate to give the pyridine and benzoylcyanocarbene (**28**) as a tight pair. The carbene would be highly electrophilic and would thus be expected to behave towards pyridine and quinoline as does, say, a sulfonylnitrene,[16] i.e., undergo addition to the nitrogen atom to give an ylide, or to the C(2)–C(3) double bond to give **29,** which would then open regiospecifically (to avoid placing a positive charge on nitrogen) to give the 3-acylalkylated product. The alternative

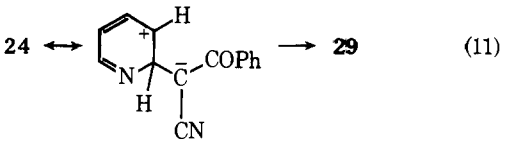
Scheme II



thermal cyclization and rearrangement of the ylide **4** to give **5** (Scheme II) could be eliminated readily when it was shown that the ylide is thermally stable.

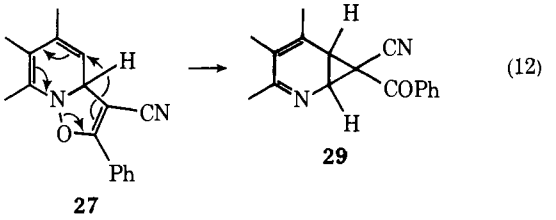
In order to test this hypothesis, authentic benzoylcyanocarbene (**28**) had to be generated in pyridine solution. It has been reported[17] that thermolysis of acylmethylene aryliodonium ylides gives ketocarbenes, while their reaction with pyridines gives pyridinium ylides.[18] Thermolysis of **16** in pyridine gave **4** (58%) in what is probably a concerted process not involving a free carbene, since no **5** was formed (see below). The required carbene precursor, benzoylcyanodiazomethane (**30**) was prepared from benzoylacetonitrile and 2-azido-3-ethylbenzothiazolium tetrafluoroborate (eq 10).[19] *p*-Toluenesulfonyl azide failed to effect diazo transfer. The expected triphenylphosphazine (**31**) was obtained from **30**. Thermolysis of **30** in pyridine gave, as expected, **4** and **5** and no **3**. On the other hand, the ylide **4** was the main product (23%), while the 3-alkylated product **5** was a minor product (2.8%), a situation exactly the opposite of that found in the phenylcyanoacetylene reaction. It appears, therefore, that while the ylides may be formed from the carbenes as suggested in Scheme II, this can at best only be a very minor route to the β-alkylated products. The alternative possibility, ring closure of **24** to **29** (eq 11),



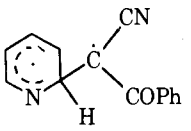


suffers from the same objections as were put forward above to the extension of the Sasaki mechanism to the *N*-oxides.

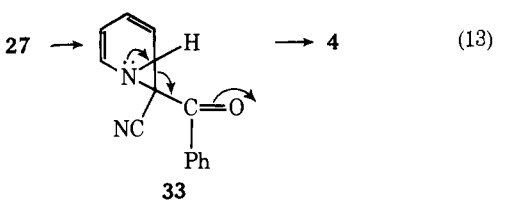
A much more likely process which overcomes these objections seems to be a concerted, symmetry allowed [$_{\sigma}2_s + {}_{\pi}2_a + {}_{\pi}4_s$] rearrangement of **27** to **29** (eq 12). The driving force for



such a ready rearrangement could be the gain in stability in replacing an N–O bond by a C–C bond, though this would be somewhat counterbalanced by the increased strain. The proposed competition between ring opening to **3** and rearrangement to **29** gets some support from the fact that if the reaction of pyridine 1-oxide and **1** is carried out in the presence of triethylamine the yield of **3** increases at the expense of that of **5**. The absence of attack at C(3) in 2-picoline 1-oxide is explained by the reluctance of cyclization to occur onto a methyl-bearing carbon in these reactions (2-methylquinoline 1-oxide, and the extremely low yield of product obtained from 2,6-lutidine 1-oxide). Thus, only the 2-methyl-1,6-dihydro intermediate would be formed, which would rearrange *only* to the 5-substituted 2-methylpyridine according to the concerted pathway, as is observed. A 2-methyl derivative of **24**, on the other hand, should have been able to undergo the proposed 1,4 shift to give the 2-methyl-3-substituted product. An alternative diradical stepwise mechanism (**32**) cannot, however, be ruled out.

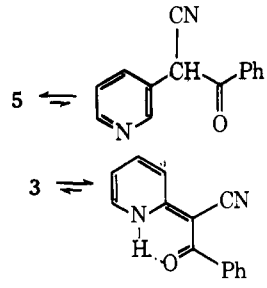


A different route to the ylides (e.g., **4**) was proposed by Hamana (eq 13).[20] This would involve a ring contraction of



27 to **33**. There are precedents for such thermal ring contractions of isoxazolines leading eventually to oxazoles.[21] No decision can be reached at this time concerning the relative merits of the two possible routes to the ylides.

Both the 2- and 3-acylalkylated products **3** and **5** could exist in different tautomeric modifications. The infrared (absence of $\nu_{C=O}$; presence of $-{}^{+}NH=$), NMR (absence of α-CH) and x-ray data indicate that the 3-substituted derivative prefers to exist in the zwitterionic form **5**, both in solution and in the solid state. The 2-acylalkylated products, on the other hand, do exhibit a carbonyl stretching band, but at lower frequency than usual (1630 cm^{-1}), indicating strong hydrogen bonding. In addition, however, they *do not* have an α-CH as shown by



3a

the NMR spectra, but do have a band at very low field (δ 16.4–17.4) which disappears on addition of D_2O. This suggests that the 2-acylalkylated products exist mainly in the strongly intramolecularly bonded form **3a**, similar to the structure proposed by Acheson and his co-workers for α-(2-pyridyl) cyanoacetates.[22]

Experimental Section

Melting points are uncorrected. Infrared spectra were measured on a Perkin-Elmer Model 257 spectrophotometer, NMR spectra on Varian HA-100 or EM-360 or Perkin Elmer R20A instruments using Me_4Si as internal standard, mass spectra on a CEC-21-104 or Hitachi Perkin-Elmer RMU-6M spectrometer at 70 eV, in the direct inlet.

Reagents. Pyridine 1-oxide and 2-, 3-, and 4-picoline 1-oxide (Reilly Tar and Chemical Corp.) were dried by azeotropic distillation with benzene. Cyanomethylpyridinium chloride had mp 176–178 °C (lit.[7] mp 178–179 °C). α-Cyanophenacylpyridinium benzoate had mp 149–150 °C (lit.[8] mp 148–150 °C) and the perchlorate salt had mp 241–243 °C dec [lit.[8] mp 242–245 °C dec]. α-Cyanophenacylpyridinium ylide (**4**) had mp 133–134 °C (from CCl_4) (lit.[9] mp 140–141 °C); mass spectrum *m/e* 222 ($M^{\cdot+}$, 54).

Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54. Found: C, 75.81; H, 4.67.

Iodosobenzene diacetate had mp 160 °C dec [lit.[23] mp 158–159 °C dec].

Phenylcyanoacetylene (1). Cyanomethyltriphenylphosphonium chloride (26.9 g) was suspended in dry benzene (500 ml) and treated with a solution of triethylamine (8.1 g) in benzene (25 ml) at room temperature with vigorous stirring (1 h). A solution of triethylamine (8.1 g) and benzoyl chloride (11.2 g) in benzene (50 ml) was now added dropwise and then stirred for 10 h at room temperature. The crystals were filtered and washed with water (2 × 15 ml). The benzene filtrate was concentrated to ca. 50 ml to give yellow crystals. The combined solids were washed with 50% aqueous EtOH (20 ml) to give α-cyanotriphenylphosphonium phenacylide (26.2 g, 81%), mp 207–209 °C (lit.[24] mp 208 °C). This was pyrolyzed at 275–280 °C (5 mm) for 1 h to give phenylcyanoacetylene (48.4%), mp 37–39 °C (lit.[24] mp 38.5–39 °C).

Reaction of Pyridine 1-Oxide with Phenylcyanoacetylene. A. In 1,2-Dichloroethane. A solution of pyridine 1-oxide (0.62 g) and phenylcyanoacetylene (0.83 g) in 1,2-dichloroethane (20 ml) was boiled under reflux for 24 h when yellow 1-cyano-2-hydroxy-2-phenyl-1-(3-pyridyl)ethylene betaine (**5**) precipitated (0.44 g, 30%): mp 237–239 °C (ethanol); ir (KBr) 2600–3340 (br, $=^+NH-$), 2190 cm^{-1} (C≡N); NMR (CF_3CO_2H) δ 9.53 (br s, 1 H, H_2), 9.04 (d, 1 H, $J_{4,5}$ = 8.9 Hz, H_4), 8.73 (d, 1 H, $J_{5,6}$ = 6.0 Hz, H_6), 8.17 (dd, 1 H, $J_{5,6}$ = 6.0, $J_{4,5}$ = 8.9 Hz, H_5), 7.70 (m, 5 H, Ph); λ_{max} (95% EtOH) 334 (ϵ 1.26 × 10^4), 279 (ϵ 5.88 × 10^3), 240 (ϵ 1.17 × 10^4); mass spectrum *m/e* 222 ($M^{\cdot+}$, 3), 105 (100), 77 (50).

Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.65; H, 4.53. Found: C, 75.54; H, 4.71.

The filtrate was evaporated in vacuo, benzene (20 ml) was added, and the red crystals which separated were recrystallized from acetone to give 1,1′-diphenyl-2,2′-dicyano-2-(3-pyridyl)divinyl ether (**6**) (0.34 g, 14.8%): mp 256–259 °C; ir (KBr) 2120, 2178 (C≡N), 1624 cm^{-1} (C=C); NMR (CF_3CO_2H) δ 9.66 (s, 1 H, H_2), 9.29 (d, 1 H, $J_{4,5}$ = 9.0 Hz, H_4), 8.82 (d, 1 H, $J_{5,6}$ = 6.0 Hz, H_6), 8.42 (dd, 1 H, $J_{4,5}$ = 9.0 $J_{5,6}$ = 6.0 Hz, H_5), 7.9–7.3 (m, 10 H, Ph), 6.70 (s, 1 H, H_α); mass spectrum *m/e* 349 ($M^{\cdot+}$, 17), 222 ($M^{\cdot+}$ − PhC≡CCN, 13), 105 (100), 77 (63).

Anal. Calcd for $C_{23}H_{15}N_3O$: C, 79.06; H, 4.32. Found: C, 79.19; H, 4.40.

The benzene filtrate was evaporated and the residue was purified by preparative TLC on silica gel PF-254 (chloroform–acetone eluent, 1:1 v/v) to give the divinyl ether (33 mg, total yield 18.1%).

B. In Benzene. A solution of pyridine 1-oxide (500 mg) and phenylcyanoacetylene (665 mg) in benzene (5 ml) was kept at room temperature for 48 h. Workup as above gave **5** (710 mg, 60.8%) and **6** (211 mg, 11.4%). The final benzene filtrate was evaporated and the residue treated with ethanol to give 2-(α-cyanophenacyl)pyridine (**3**) (24 mg, 2.5%): mp 155–157 °C; ir (KBr) 2190 (C≡N), 1630 cm^{-1} (C=O); NMR ($CDCl_3$) δ 17.4 (s, 1 H, exchanges with D_2O, NH), 7.88–7.68 (m, 4 H, H_4, H_6, and phenyl *o*-H), 7.54 (d, $J_{3,4}$ = 9.0 Hz, H_3), 7.43 (m, 3 H, Ph), 6.93 (m, 1 H; H_5); mass spectrum *m/e* 222 ($M^{\cdot+}$, 84), 221 ($M^{\cdot+}$ − 1, 99), 145 ($M^{\cdot+}$ − Ph, 39), 105 (47), 77 (100).

Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.65; H, 4.53. Found: C, 75.88; H, 4.56.

The ethanol filtrate was evaporated and the residue purified by preparative TLC (silica gel PF-254, chloroform–acetone 1:1 v/v as eluent) to give α-cyanophenacylpyridinium ylide (**4**) (4 mg, 0.4%), mp 131–133 °C dec (CCl_4), identical with an authentic sample prepared as described above.

C. In Benzene in the Presence of Acid. The reaction was carried out as above except that 3 drops of acetic acid were added to the solution, which was then boiled under reflux for 24 h to give **5** (59.9%), **6** (12.5%), **3** (1.28%), and α-cyanophenacylpyridinium ylide (**4**) (2.1%).

D. In Benzene in the Presence of Triethylamine. The reaction was repeated in benzene as under **C**, except that triethylamine (1.05 mmol) was added and the solution boiled under reflux for 10 h. Thus were obtained **5** (9.8%), **6** (26.3%), and **3** (7.7%).

Reaction of 5 with Phenylcyanoacetylene. A solution of **5** (10 mg) and **1** (6 mg) in ethanol (5 ml) containing 1 drop of triethylamine was allowed to stand at room temperature for 2 h. The solvent was concentrated down to ca. 1 ml when the divinyl ether (**6**) separated (14.6 mg, 93%), mp 255–259 °C dec, identical with the compound obtained above.

Reaction of 5 with Methyl Propiolate. A solution of **5** (22 mg) and methyl propiolate (10 mg) in ethanol (7 ml) was boiled under reflux for 10 h. The solvent was evaporated and the residue treated with acetone–light petroleum (bp 80–110 °C) to give red crystals of 2-cyano-2′-methoxycarbonyl-1-phenyl-2-(3-pyridyl)divinyl ether (**8**) (25 mg, 81.5%): mp 214–215 °C dec; ir (KBr) 2165 (C≡N); 1730, 1720 (C=O), 1655 cm^{-1} (C=C); NMR (CF_3CO_2H) δ 9.62 (s, 1 H, H_2) 9.08 (d, 1 H, $J_{4,5}$ = 9.0 Hz, H_4), 8.86 (d, 1 H, $J_{5,6}$ = 6.0 Hz, H_6), 8.51 (d, 1 H, J_{AB} = 14.0 Hz, H_B), 8.20 (dd, 1 H, $J_{5,6}$ = 6.0, $J_{4,5}$ = 9.0 Hz, H_5), 7.40–7.80 (m, 5 H, Ph), 7.04 (d, 1 H, J_{AB} = 14.0 Hz, H_A), 4.0 (s, 3 H, OCH_3).

Anal. Calcd for $C_{18}H_{14}N_2O_3$: C, 70.58; H, 4.61. Found: C, 70.40; H, 4.65.

2-Cyano-1-methoxy-2-(3-pyridyl)styrene (9). A solution of **5** (62 mg) in ethanol (10 ml) was stirred with potassium carbonate (38.5 mg) for 20 min at room temperature and then treated with a solution of methyl iodide (40 mg) in ethanol (2 ml). The mixture was stirred for 18 h at room temperature, the solvent was evaporated, water (10 ml) was added, and the mixture was extracted with benzene (3 × 10 ml). The extracts were washed with water (5 ml), dried (Na_2SO_4), and evaporated, and the residue was treated with carbon tetrachloride (5 ml) to give the yellow *O*-methyl ether (**9**) (40 mg, 60.5%): mp 199–200 °C dec (acetone); ir, no carbonyl stretching band; NMR (acetone-d_6) δ 8.3 (m, 2 H, H_2, H_6), 7.3–7.9 (m, 7 H, Ph, H_4, H_5), 4.42 (s, 3 H, OCH_3); mass spectrum *m/e* 236 ($M^{\cdot+}$, 42).

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12. Found: C, 76.40; H, 5.28.

Hydrolysis of 5. The nitrile (0.20 g) was boiled with KOH (0.45 g) in water (20 ml) for 1 h, the solution was acidified with 10% HCl, and extracted with $CHCl_3$ (3 × 10 ml). The extract was dried (Na_2SO_4), filtered, and concentrated to give benzoic acid (0.089 g, 80%). The aqueous layer was evaporated to dryness and suspended in methanol (75 ml), 30% H_2SO_4 (2 drops) was added, and the mixture was boiled under reflux for 24 h. The solvent was evaporated, water (10 ml) was added, and the solution was neutralized with solid $NaHCO_3$. Extraction with $CHCl_3$ (3 × 10 ml) and drying ($CaCl_2$) and concentrating the extract gave methyl 3-pyridylacetate (0.11 g, 77%), whose infrared spectrum was identical with that of an authentic sample.

1-Cyano-2-hydroxy-2-phenyl-1-(3-pyridyl)ethylene (5). Ethyl benzoate (2.55 g) was added to a solution of sodium (0.39 g) in ab-

solute ethanol (15 ml). The mixture was stirred and boiled under reflux and dry (molecular sieve type 4A) 3-pyridylacetonitrile (2.0 g) was added dropwise. Boiling under reflux was continued for 48 h, the ethanol was distilled off, and the residual oil was dissolved in water (10 ml). The solution was extracted with $CHCl_3$ (3 × 10 ml) and the aqueous layer neutralized with 10% HCl to give the desired 3-pyridylethylene derivative (2.60 g, 69%), mp 238–239 °C (95% ethanol), identical with the compound obtained above.

2-(α-Cyanophenacyl)pyridine (3). Benzoylacetonitrile (5.0 g) in acetic anhydride (15 ml) was added dropwise with stirring to pyridine 1-oxide (3.5 g) in acetic anhydride (5 ml) at 0 °C. The mixture was stirred at 0° for 2 h and then at room temperature for 36 h. The excess anhydride was distilled off at 40–50 °C (0.5 mm) and the last traces removed by distillation with benzene. Chloroform (15 ml) was added, and the solution was washed with excess aqueous $NaHCO_3$ and extracted with 10% KOH (3 × 50 ml) at 0°. The aqueous layer was acidified with glacial acetic acid and extracted with $CHCl_3$ (3 × 15 ml), the extract was dried (Na_2SO_4), filtered, and evaporated in a stream of air. Fractional recrystallization of the solid residue from CCl_4 gave unreacted benzoylacetonitrile (0.5 g, 10%), and 2-(α-cyanophenacyl)pyridine (**3**) (0.047 g, 0.6%), mp 159–160 °C (from benzene–light petroleum), identical with the sample obtained above.

Attempted Thermal Rearrangement of α-Cyanopyridinium Phenacylide (4). The ylide (**4**) was heated in various solvents (1,2-dichloroethane, acetonitrile, *p*-dioxane, acetonitrile–triethylamine, benzene) for various lengths of time (24–50 h) but was invariably recovered quantitatively.

Reaction of α-Cyanophenacylphenyliodonium Ylide (16) with Pyridine Bases. To a solution of benzoylacetonitrile (300 mg) and potassium hydroxide (348 mg) in methanol (10 ml) was added finely powdered iodosobenzene diacetate (670 mg) portionwise at −4 to −5 °C over a period of 15 min with stirring. The mixture was stirred for another hour, ice water (15 ml) was added, and the ylide **16** [(590 mg, 82%); mp 85–88 °C dec] which separated was filtered, washed with light petroleum (bp 60–110 °C) (20 ml), and used as such. Because of its instability a reliable analysis for carbon and hydrogen could not be obtained.

A. With Pyridine. To a stirred solution of the ylide **16** (500 mg) in dry 1,2-dichloroethane (5 ml) was added pyridine (120 mg) dropwise at 0 °C and the mixture was then stirred for 1 h at room temperature. The solvent was evaporated and the residue was treated with CCl_4 to give α-cyanopyridinium phenacylide (186 mg, 58%), mp 133–134 °C (from CCl_4), identical with the authentic sample. No 3-alkylated product (**5**) could be detected by TLC.

B. With Quinoline. The dried (explosive) iodonium ylide (260 mg) and quinoline (200 mg) in 1,2-dichloroethane (6 ml) were stirred for 2 h at room temperature and then an additional hour at 40–45 °C. The solvent was evaporated and the residue was chromatographed on a column of silica gel (2.0 × 15 cm). Elution with $CHCl_3$ gave α-cyanoquinolinium phenacylide (**15**) (38 mg, 20.4%) as red needles: mp 222–223 °C (from ethanol); ir (KBr) 2170 (C≡N), 1621, 1543 cm^{-1}; NMR ($CDCl_3$) δ 9.16 (dd, 1 H, $J_{2,3}$ = 6, $J_{2,4}$ = 1.0 Hz, H_2), 8.68 (m, 2 H, H_4, H_8), 7.45–8.18 (m, 9 H, ArH); mass spectrum *m/e* 272 ($M^{\cdot+}$, 68), 271 ($M^{\cdot+}$ − 1, 86), 105 (79), 77 (100).

Anal. Calcd for $C_{18}H_{12}N_2O$: C, 79.39; H, 4.44. Found: C, 79.28; H, 4.49.

C. With Isoquinoline. The reaction was carried out as above, but with isoquinoline to give α-cyanoisoquinolinium phenacylide (**17**) (83%): mp 209–210 °C dec; ir (KBr) 2162, 1635, 1540 cm^{-1}; NMR ($CDCl_3$) δ 10.40 (s, 1 H, H_1), 8.77 (d, 1 H, $J_{3,4}$ = 7.0 Hz, H_3), 7.38–8.2 (m, 10 H, ArH); mass spectrum *m/e* 272 ($M^{\cdot+}$, 74), 271 ($M^{\cdot+}$ − 1, 100), 105 (12), 77 (21).

Anal. Calcd for $C_{18}H_{12}N_2O$: C, 79.39; H, 4.44. Found: C, 79.55; H, 4.56.

Hydrolysis of 1,1′-Diphenyl-2,2′-dicyano-2-(3-pyridyl)divinyl Ether. A solution of **6** (300 mg) in 15% HCl was stirred for 3 h at room temperature. The solution was extracted with ether (3 × 50 ml), the extract evaporated, and the residue treated with CCl_4 to give benzoylacetonitrile (14 mg, 9.4%), mp 78–80 °C (lit.[25] mp 79–80 °C). The acidic layer was neutralized with $NaHCO_3$ to give **5** (61 mg, 32%), mp 237–239 °C.

Reaction of 2-Picoline 1-Oxide with Phenylcyanoacetylene. A solution of 2-picoline 1-oxide (500 mg) and phenylcyanoacetylene (585 mg) in benzene (5 ml) was kept at room temperature for 24 h. The orange-yellow crystals which separated were filtered and recrystallized from EtOH to give 1-cyano-2-hydroxy-2-phenyl-1-(2-methyl-5-pyridyl)ethylene betaine (**12**) (469 mg, 43.4%): mp 237–239 °C; ir (KBr) 2800–2500, 2160, 1620 cm^{-1}; NMR (CF_3CO_2H) δ 9.52 (s, 1 H, H_6), 9.00 (d, 1 H, $J_{3,4}$ = 8.0 Hz, H_4), 8.15 (d, 1 H, $J_{3,4}$ = 8.0 Hz, H_3), 7.9 (m, 5 H, phenyl), 3.15 (s, 3 H, CH_3); mass spectrum *m/e* 236 ($M^{\cdot+}$, 7.7), 235 ($M^{\cdot+}$ − H, 3.5), 158 (3.9), 131 ($M^{\cdot+}$ − PhCO, 35.4), 105 (100), 77 (64).

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12. Found: C, 76.27; H, 5.18.

Reaction of 3-Picoline 1-Oxide with Phenylcyanoacetylene. The reaction was carried out as for 2-picoline 1-oxide and gave 1,1′-diphenyl-2,2′-dicyano-2-(3-methyl-5-pyridyl)divinyl ether (**10**; R = 5-Me) (520 mg, 31.3%): mp 235–236 °C dec (ethanol); ir (KBr) 2210, 2160, 1610 cm^{-1}; NMR (CF_3CO_2H) δ 9.52 (s, 1 H, H_6), 9.10 (s, 1 H, H_2), 8.61 (s, 1 H, H_4), 7.8–7.3 (m, 10 H, phenyl), 6.69 (s, 1 H, H_α), 2.79 (s, 3 H, CH_3); mass spectrum *m/e* 363 ($M^{\cdot+}$, 0.74), 236 ($M^{\cdot+}$ − PhC≡CCN, 6.3), 127 (PhC≡CCN, 34), 105 (100), 77 (54).

Anal. Calcd for $C_{24}H_{17}N_3O$: C, 79.32; H, 4.72. Found: C, 79.37; H, 4.75.

Reaction of 4-Picoline 1-Oxide with Phenylcyanoacetylene. Carried out as above, this gave 1,1′-diphenyl-2,2′-dicyano-2-(4-methyl-3-pyridyl)divinyl ether (27.7%): mp 135–136 °C dec (from ethanol–light petroleum); ir (KBr) 2220, 2160, 1620 cm^{-1}; NMR (CF_3CO_2H) δ 9.46 (s, 1 H, H_2), 9.18 (d, 1 H, $J_{5,6}$ = 6.0 Hz, H_6), 8.26 (d, 1 H, $J_{5,6}$ = 6.0 Hz, H_5), 7.9–7.2 (m, 10 H, phenyl), 6.65 (s, 1 H, H_α), 2.96 (s, 3 H, CH_3); mass spectrum *m/e* 363 ($M^{\cdot+}$).

Anal. Calcd for $C_{24}H_{17}N_3O \cdot \frac{1}{2}H_2O$: C, 77.40; H, 4.87. Found: C, 77.34; H, 5.12.

Reaction of 3,5-Lutidine 1-Oxide with Phenylcyanoacetylene. Carried out as above using 3,5-lutidine 1-oxide[26] at 70–75 °C for 4 h, this gave 2-(α-cyanophenacyl)-3,5-dimethylpyridine (**11**) (77.2%): mp 186–187 °C (from ethanol); ir (KBr) 2180, 1631 cm^{-1}; NMR ($CDCl_3$) δ 7.83 (d, 1 H, $J_{4,6}$ = 2.8 Hz, H_6), 7.75 (d, 1 H, $J_{4,6}$ = 2.8 Hz, H_4), 7.64 (s, 1 H, H_α), 7.5–7.3 (m, 5 H, phenyl), 2.71 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3); mass spectrum *m/e* 250 ($M^{\cdot+}$).

Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64. Found: C, 76.65; H, 5.68.

Reaction of 3,4-Lutidine 1-Oxide[27] with Phenylcyanoacetylene. Carried out as above (36 h at room temperature) and purification of the product by TLC (acetone–CCl_4, 1:1 v/v as eluent), the reaction gave 1,1′-diphenyl-2,2′-dicyano-2-(4,5-dimethyl-3-pyridyl)divinyl ether (**10**; R = 4,5-Me_2) (4%): mp 156–157 °C (acetone); ir (KBr) 2220, 2150 cm^{-1}; NMR (CF_3CO_2H) δ 9.68 (s, 1 H, H_6), 9.12 (s, 1 H, H_2), 7.6–7.2 (m, 10 H, phenyl), 6.80 (s, 1 H, H_α), 3.18 (s, 3 H, 4-Me), 2.93 (s, 3 H, 3-Me); mass spectrum *m/e* 377 ($M^{\cdot+}$).

Anal. Calcd for $C_{25}H_{19}N_3O \cdot H_2O$: C, 75.93; H, 5.35. Found: C, 76.05; H, 5.46.

Reaction of 2,6-Lutidine 1-Oxide with Phenylcyanoacetylene. After heating in benzene at 90 °C (sealed tube) for 10 h and chromatography on a column of alumina, this gave 1,1′-diphenyl-2,2′-dicyano-2-(2,6-dimethyl-3-pyridyl)divinyl ether (**10**; R = 2,6-Me_2) (3%): mp 224–225 °C dec (from ethanol); ir (KBr) 2240, 2195, 1625 cm^{-1}; NMR (CF_3CO_2H) δ 8.72 (d, 1 H, $J_{4,5}$ = 9.2 Hz, H_4), 8.31 (d, 1 H, $J_{4,5}$ = 9.2 Hz, H_5), 7.81–7.13 (m, 10 H, phenyl), 6.84 (s, 1 H, H_α), 3.28 (s, 3 H, CH_3), 3.18 (s, 3 H, CH_3); mass spectrum *m/e* 377 ($M^{\cdot+}$, 3.5), 250 ($M^{\cdot+}$ − PhC≡CCN, 56).

Anal. Calcd for $C_{25}H_{19}N_3O$: C, 79.55; H, 5.07. Found: C, 79.50; H, 5.08.

Reaction of Quinoline 1-Oxide with Phenylcyanoacetylene. A solution of phenylcyanoacetylene (480 mg) and anhydrous quinoline 1-oxide (500 mg) in 1,2-dichloroethane (30 ml) was boiled under reflux for 12 h and then kept at room temperature overnight. 1-Cyano-2-hydroxy-2-phenyl-1-(3-quinolyl)ethylene (**13**) (241 mg, 25.7%) precipitated as an orange-red solid: mp 264–265 °C dec (from ethanol); ir (KBr) 2700–2400 ($^+$NH), 2205, 2170, 1621, 1575 cm^{-1}; NMR (C_5D_5N) δ 9.94 (br d, 1 H, *J* = 2 Hz), 8.96–7.06 (m, 11 H); mass spectrum *m/e* 272 ($M^{\cdot+}$, 6.1), ($M^{\cdot+}$ − 1, 19.5), 105 (100), 77 (35).

Anal. Calcd for $C_{18}H_{12}N_2O$: C, 79.39; H, 4.44. Found: C, 79.44; H, 4.49.

Evaporation of the solvent from the reaction mixture followed by chromatography on a column of silica gel (2 × 25 cm) gave, on elution with benzene–chloroform (1:3 v/v), benzoyl(2-quinolyl)acetonitrile (**14**) (106 mg, 11.3%), mp 203–204 °C (from ethanol), identical with an authentic sample prepared as described below; ir (KBr) 2192 (C≡N), 1635 cm^{-1} (C=O); NMR ($CDCl_3$) δ 16.4 (br s, 1 H, D_2O

exchange, NH), 8.73 (d, 1 H, $J_{3,4}$ = 9 Hz, H_4), 8.30–7.20 (m, 10 H, ArH); mass spectrum *m/e* 273 ($M^{\cdot+}$ + 1, 19), 272 ($M^{\cdot+}$, 100), 271 (37), 195 (45), 105 (32), 77 (63).

Anal. Calcd for $C_{18}H_{12}N_2O$: C, 79.39; H, 4.44. Found: C, 79.53; H, 4.52.

Further elution with chloroform gave the ylide **15** (75 mg, 8%), identical with the authentic sample prepared above.

Benzoyl(2-quinolyl)acetonitrile (14). To a stirred solution of quinoline 1-oxide (1.45 g) in acetic anhydride (2.5 g) was slowly added benzoylacetonitrile (1.45 g) at 0 °C over a period of 30 min. The mixture was stirred at 50 °C for 7 h, made basic with 10% aqueous sodium carbonate, and extracted with $CHCl_3$ (10 ml). The solvent was evaporated and the residue chromatographed on silica gel (100 g). Elution with light petroleum–chloroform–acetone (9:3:1 v/v) gave the desired benzoyl(2-quinolyl)acetonitrile (0.10 g, 3.1%), mp 206–207 °C, identical with the sample obtained above.

Reaction of Isoquinoline 1-Oxide with Phenylcyanoacetylene. A solution of isoquinoline 1-oxide (0.57 g) and phenylcyanoacetylene (0.50 g) in carbon tetrachloride (25 ml) was boiled under reflux for 24 h to give the ylide **18** (0.678 g, 63%), mp 209–210 °C dec, identical with the authentic sample prepared above.

Benzoylcyanodiazomethane (30). A solution of benzoylacetonitrile (500 mg) in 90% ethanol (15 ml) was added dropwise to a stirred solution of 2-azido-3-ethylbenzothiazolium tetrafluoroborate[19] (1.0 g) in 90% ethanol (15 ml) over a period of 10 min. The solution was stirred for 16 h at room temperature, poured into ice water (400 ml), and extracted with ether (4 × 30 ml). The extract was washed with ice water (3 × 20 ml), then with 1 N HCl (2 × 10 ml), again with ice water (2 × 20 ml), and dried (Na_2SO_4), and then evaporated in vacuo. The orange crystals (470 mg, 79%) so obtained were purified by TLC on silica gel PF-254 (chloroform developer) and recrystallized from light petroleum to give **30** (430 mg, 72.1%): mp 47–48 °C dec; ir (KBr) 2220, 2170, 2140, 1630 cm^{-1}; mass spectrum, *m/e* 171 ($M^{\cdot+}$).

Anal. Calcd for $C_9H_5N_3O$: C, 63.16; H, 2.94. Found: C, 63.25; H, 2.94.

A solution of **30** in benzene was treated with triphenylphosphine to give the triphenylphosphazine (**31**) (53.4%), mp 162–163 °C dec.

Anal. Calcd for $C_{27}H_{20}N_3OP$: C, 74.83; H, 4.62. Found: C, 74.76; H, 4.69.

Decomposition of 30 in Pyridine. A solution of benzoylcyanodiazomethane (300 mg) and pyridine (170 mg) in 1,2-dichloroethane (50 ml) was boiled under reflux for 7.5 h. The solvent was evaporated and the residue treated with ethanol (2 ml) to give **5** (11 mg, 2.8%), mp 235–238 °C (from ethanol), identical with an authentic sample. The filtrate was evaporated and the residue purified by TLC on silica gel PF-254 (chloroform–acetone 1:1 v/v developer) to give **4** (90 mg, 23%), mp 133–134 °C, identical with an authentic sample.

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