tention time of 24.8 min. The second peak (retention time, 26.3 min) was due to the *r*-1,*t*-3,*t*-4-ester (11) identical with the material previously obtained[1]). No side products were formed. Esterification runs on individual acids indicated these to be essentially quantitative.

The results, which are the averages of two runs, are summarized in Table IV.

Table IV
Equilibration of the *r*-1,*t*-3,*t*-4-Dicarboxylic Acid with 12 *N* Hydrochloric Acid

T, °K	*r*-1, *t*-3, *t*-4 : *r*-1, *t*-3, *c*-4	K_{eq}
451 ± 2	92 : 8 (±1%)	11.5 ± 0.2
471 ± 2	90 : 10 (±1%)	9.0 ± 0.2
490 ± 2	88.5 : 11.5 (±1%)	7.7 ± 0.2

$\Delta H°$ and $\Delta S°$ were determined graphically using the following equations.

$$\Delta H° = \frac{-R[\ln K_2 - \ln K_1]}{(1/T_2) - (1/T_1)}$$

$$\Delta S° = \frac{RT_2 \ln K_2 - RT_1 \ln K_1}{T_2 - T_1}$$

$$\Delta H° = -4.3 \pm 0.1 \text{ kcal/mol}$$

$$\Delta S° = 4.8_5 \pm 0.02 \text{ eu}$$

$$\Delta G°_{25} = \Delta H° - T\Delta S° = -2.9 \pm 0.1 \text{ kcal/mol}$$

Equilibration of Dicarboxylic Acids 15 and 16. (a) With 5% Aqueous Sodium Hydroxide (*cf.* ref 18). Each of the pure acids (0.014–0.018 g) was placed in a Pyrex tube and treated with an excess of 5% NaOH solution (0.3 ml): the tubes were sealed and heated at 240 ± 4° for 24 hr. The solutions were acidified and evaporated to dryness, the residue was esterified with diazomethane,[1] and the esters were analyzed by glc as described above.

(b) With 12 *N* HCl. This was carried out as described above for the equilibration of **14**. The infrared spectrum of the crude reaction mixture indicated the lack of formation of any cyclic or other acid anhydride, as also did glc. The crude acids were methylated with diazomethane [as under (a) above] and analyzed.

(c) With 10% Palladium on Charcoal (*cf.* ref 19). Each of the pure acids (0.02–0.03 g) was mixed with 10% Pd–C (0.007 g) and heated in a sealed tube at 240 ± 4° for 29 hr. The products were extracted with ether (2 (2 ml) and centrifuged, and the solution was decanted (procedure repeated twice). Again no anhydride was formed. Methylation with diazomethane was followed by quantitative glc analysis.

In none of the above cases were any by-products formed nor was any evidence found that one conformer was being selectively consumed. The results are summarized in Table III.

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Registry No.—**1**, 7370-14-1; **7**, 23022-33-5; **8**, 53154-24-8; **9**, 23191-42-6; **10**, 23191-41-5; **11**, 53154-25-9; **12**, 53154-26-0; **13**, 53154-27-1; **14**, 18680-01-8; **15**, 18679-93-1; **16**, 18679-94-2; 4-*tert*-butylcyclohexene-1-carboxylic acid, 31845-19-9; diethyl malonate, 105-53-3.

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The Direct Acylamination of Quinoline, Isoquinoline, Benzimidazole, Pyridazine, and Pyrimidine 1-Oxides. A Novel 1,5-Sigmatropic Shift[1]

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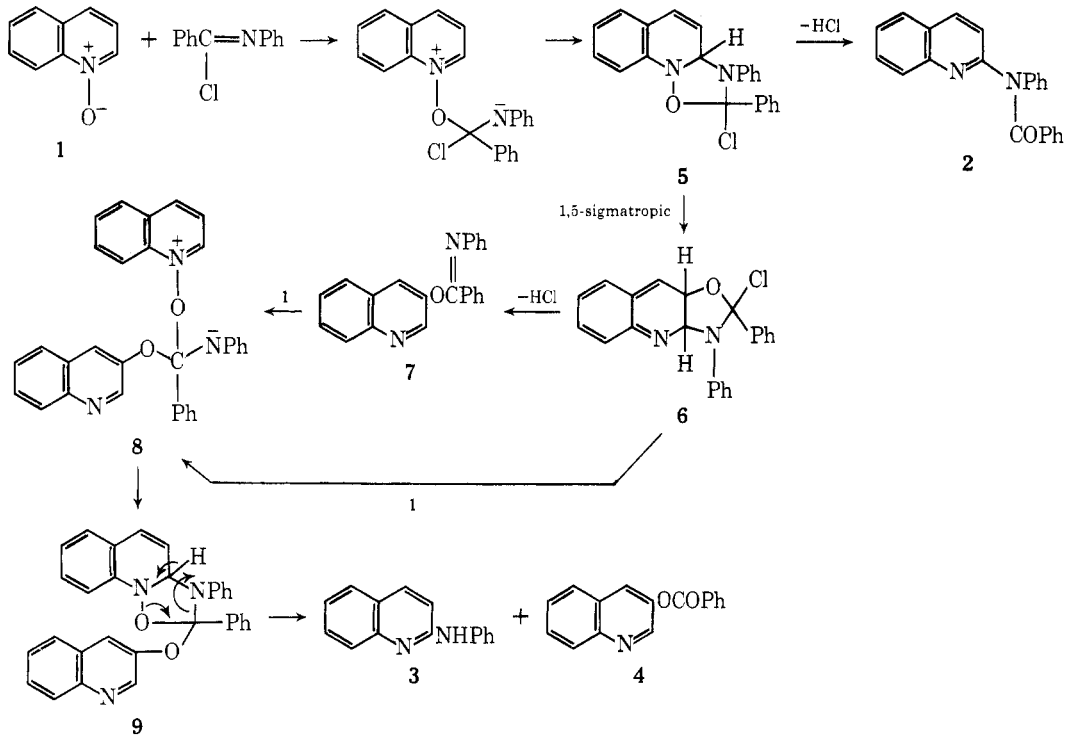
The direct acylamination of pyridine 1-oxides using an *N*-phenylbenzimidoyl chloride or the corresponding nitrilium salt has been extended to the title heteroaromatic *N*-oxides. With quinoline 1-oxide it is proposed that a novel 1,5-sigmatropic shift in the 1,2-dihydro intermediate eventually led to 3-quinolyl benzoate and to 2-anilinoquinoline. 2,6-Lutidine similarly gave 3-(2,6-dimethylpyridyl)-*N*-phenylbenzimidate. The possible mechanisms of the formation of these products are discussed.

The direct acylamination of pyridine 1-oxides using imidoyl halides or nitrilium salts has recently been reported.[2] The main by-products formed when *N*-phenylbenzimidoyl chloride was used were the corresponding 3-chloropyridine derivative and benzanilide. The present paper describes the extensions of this work to other heterocyclic systems.

Acylamination of 6-methyl- and 4,6-dimethylpyrimidine 1-oxides with *N*-phenylbenzimidoyl chloride gave low to moderate yields of the expected 2-*N*-benzoylanilino derivative together with some of the debenzoylated secondary amine (no attempt was made to optimize yields in these reactions; we believe that much higher yields of products are possible). In addition to being a synthetically useful approach to substituted 2-acylaminated pyrimidines this reaction could, in principle, be used to differentiate between isomeric unsymmetrically substituted pyrimidine 1-

Scheme I



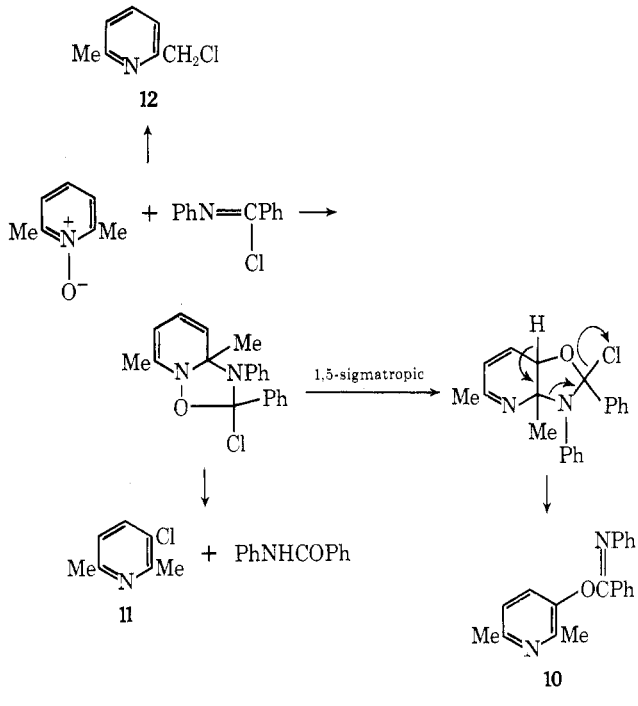
oxides and would thus complement the nmr technique for doing so. For example, 4-methylpyrimidine 1-oxide might be expected to give a mixture of both 2- and 6-acylaminated products, while 6-methylpyrimidine 1-oxide can only give the 2-acylaminated product.

Pyridazine 1-oxide gave 3-*N*-benzoylanilinopyridazine which, in contrast to the other tertiary amides, proved to be rather stable to hydrolysis by hot aqueous acid. Isoquinoline 1-oxide and *N*-phenylbenzimidoyl chloride gives the expected 1-acylaminated product together with a moderate yield of 4-chloroisoquinoline and of benzanilide.

The proposed mechanism[2] for the acylamination indicates that the reaction only depends on the presence in the substrate molecule of a nitrone function, and not on the substrate being a six-membered heteroaromatic *N*-oxide. Thus, benzimidazole *N*-oxides should behave similarly and, indeed, 2-*N*-benzoylanilino-1-benzylbenzimidazole could be prepared in high yield from 1-benzylbenzimidazole 3-oxide and *N*-phenylbenzimidoyl chloride. The amide underwent hydrolysis to the secondary amine on standing in a stoppered vial for some time. The results of these acylaminations are summarized in Table I. A possible explanation of the wide variation in product yields under comparable conditions is that the lower the basicity of the *N*-oxide function the slower the initial addition to the imidoyl chloride and the lower the yield of desired product. Some support for this comes from the fact that no acylamination product could be obtained from 4-nitropyridine 1-oxide.[2a] This suggests that longer reaction times may be beneficial in these cases.

The reaction of anhydrous quinoline 1-oxide (1) with *N*-phenylbenzimidoyl chloride led to some unexpected results. In addition to 2-*N*-benzoylanilinoquinoline (2) and benzanilide there were obtained about equal amounts of 2-anilinoquinoline (3) (35.8%) and 3-quinolyl benzoate (4) (33.5%) under completely anhydrous conditions and prior to hydrolysis. That 3 was not being formed from 2 under the reaction conditions was established by showing that 2 was stable under these conditions and that 2, 3, and 4 were being formed simultaneously right from the beginning

Scheme II



(course of the reaction followed with time by gas chromatographic analysis).

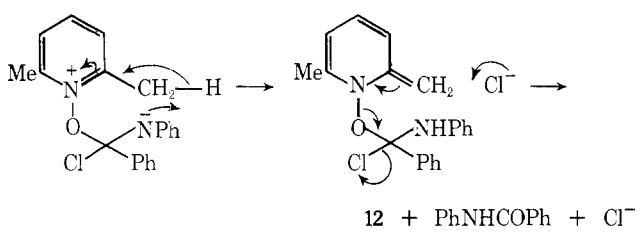
Since the reaction was carried out in the complete absence of air or any other source of oxygen both oxygen atoms in 4 must come from quinoline 1-oxide. A possible mechanism of the formation of 4 and the simultaneous generation of 3 is outlined in Scheme I. The key feature of this proposal is a 1,5-sigmatropic shift of the initial 1,2-dihydroquinoline intermediate (5) to give a 2,3-dihydro derivative (5). Aromatization of the latter would give 3-quinolyl *N*-phenylbenzimidate (7). This could conceivably react with more *N*-oxide to give an adduct (8) which would then undergo intramolecular cyclization to 9 that would aromat-

Table I
Reaction of Various Heteroaromatic *N*-Oxides with *N*-Phenylbenzimidoyl Chloride

N-Oxide	Registry No.	Products	Registry No.	% Yield[a]
6-Methylpyrimidine 1-oxide	33342-83-5	2-*N*-Benzoylanilino-4-methylpyrimidine	53112-25-7	1.5
		2-Anilino-4-methylpyrimidine	53112-26-8	11.5
		Benzanilide		33
4,6-Dimethylpyrimidine 1-oxide	14161-42-3	2-*N*-Benzoylanilino-4,6-dimethylpyrimidine	53112-27-9	22
		2-Anilino-4,6-dimethylpyrimidine	53112-28-0	9
		Benzanilide		29
Pyridazine 1-oxide[c]	1457-42-7	3-*N*-Benzoylanilinopyridazine	53112-29-1	18
		Benzanilide		5.3
1-Benzylbenzimidazole 3-oxide	27430-55-3	2-*N*-Benzoylanilino-1-benzylbenzimidazole	24068-32-4	92
Isoquinoline 1-oxide	1532-72-5	1-*N*-Benzoylanilinoisoquinoline	53112-30-4	55[b]
		4-Chloroisoquinoline		23[b]
		Benzanilide	1532-91-8	42[b]

[a] Isolated yields. [b] Gas chromatographic yields. [c] With *N*-phenylbenzonitrilium hexachloroantimonate.

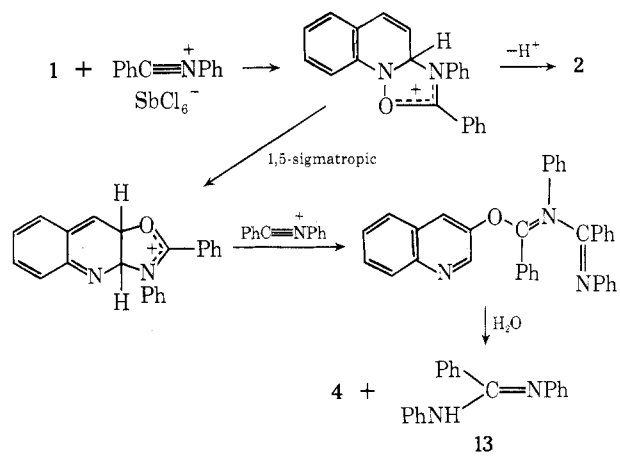
ize to give **3** and **4**. Alternatively, **6** could react with **1** directly to give **8**. The latter appears to be the more likely possibility, for when authentic imidate **7** was prepared from the sodium salt of 3-hydroxyquinoline and *N*-phenylbenzimidoyl chloride and treated with **1** or 1-hydrochloride no **3** or **4** were formed. On the other hand, formation of **7** is not unreasonable. Indeed, we have found that in the pyridine 1-oxide series if the 2 and 6 positions are blocked by methyl groups so that aromatization of the 1,2-dihydro intermediate is not possible then the 1,5-sigmatropic shift occurs readily and gives *O*-(2,6-dimethyl-3-pyridyl)-*N*-phenylbenzimidate (**10**) (37%), together with some 3-chloro-2,6-lutidine (**11**) (21%),[4] 2-chloromethyl-6-methylpyridine (**12**) (12%), and benzanilide (45%) (Scheme II). Similar results were obtained contemporaneously by Parham and Sloan[3] who extended the work to 2,4-dimethylquinoline. The formation of the 3-chloro compound (**11**) and benzanilide can be explained by the mechanism proposed earlier.[2a] The side chain chlorinated compound probably arises by intramolecular hydrogen abstraction by the intermediate anion followed by intra- or intermolecular nucleophilic addition of chloride ion (only inter- shown). This is mechanistically



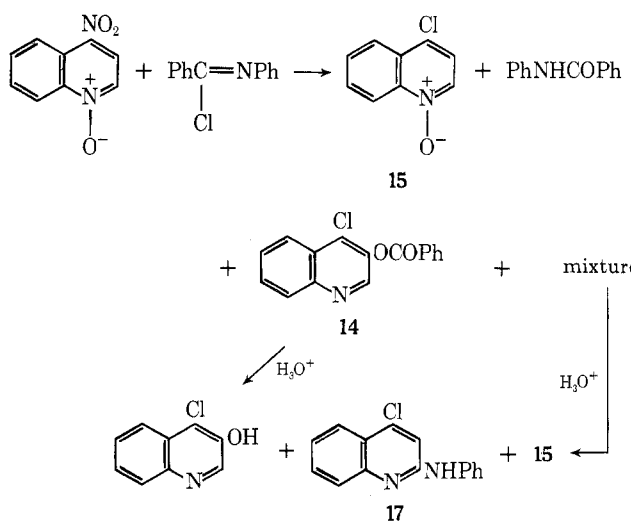
similar to the side-chain chlorination of 2-picoline 1-oxides by tosyl chloride.[5]

When quinoline 1-oxide was treated with *N*-phenylbenzonitrilium hexachloroantimonate a vigorous reaction occurred which was not as clean as the one in which the imidoyl chloride was used. Quenching the mixture with water gave **2** (5%), benzanilide (25%), **4** (20%), and *N,N'*-diphenylbenzamidine (**13**) (10%). No **3** was detected. A possible route to these products is outlined in Scheme III, though **13** could conceivably arise from benzanilide and nitrilium salt (which would not, however, explain the absence of **3**).

Scheme III



The reaction of 4-nitroquinoline 1-oxide with *N*-phenylbenzimidoyl chloride gave a number of products only four of which have been characterized: benzanilide, 4-chloro-3-quinolyl benzoate (**14**),[6] 4-chloroquinoline 1-oxide (**15**), and an oily mixture which could not be resolved but which, on boiling with 4 *N* HCl, gave **15**, 4-chloro-3-hydroxyquino-



line (**16**) (also obtained by hydrolysis of **14**), and 2-anilino-4-chloroquinoline (**17**), together with tars. The structure of **14** was deduced from its spectral properties (ester C=O stretch at 1745 cm^{-1} and strong band at 1255 cm^{-1}; $^{35}M^{\cdot+}$ *m/e* 283, $^{37}M^{\cdot+}$ *m/e* 285; *m/e* 105 (100) ($PhCO^+$), nmr δ 8.81, s, H_2), its hydrolysis to 4-chloro-3-hydroxyquinoline (ν_{OH} in ir, no C=O), and on the reasonable assumption that the chlorine substituent is introduced by nucleophilic displacement of the 4-nitro group either in the parent *N*-oxide or, more likely, in the initial *O*-acylated product. 2-Anilino-4-chloroquinoline (**17**) is a known compound[7] and had the expected spectral properties.

It is interesting to note that the formation of 3-substituted pyridyl or quinolyl esters in the reaction between pyridine or quinoline 1-oxide and 2-bromopyridine or 2-bromoquinoline[8] may be explained[9] by invoking a 1,5-sigmatropic shift similar to that postulated above.

Experimental Section

Reactants and solvents were purified prior to use either by recrystallization or distillation. Solvents were dried and distilled prior to use. Thus, all halocarbon solvents were boiled under reflux for 12 hr over phosphorus pentoxide and then distilled. Anhydrous diethyl ether was used directly from freshly opened cans. Tetrahydrofuran was purified by distillation from calcium hydride and then from lithium aluminum hydride. Light petroleum refers to that fraction with a boiling range of 60–110°, unless specified otherwise.

All nuclear magnetic resonance spectra were determined using a Varian Associates model HA-100 spectrometer. Mass spectra were recorded on a C.E.C. Model 21-104 spectrometer, usually at an ionizing voltage of 70 eV. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrometer. Solid compounds were run as KBr discs while liquids were run as liquid films. Each spectrum was calibrated using polystyrene as a reference at 1944 and 906 cm^{-1}. Melting points are uncorrected. Gas chromatographic analyses were carried out using a Varian Associates Model 200 with helium as the carrier gas. They were performed using dual columns (7 ft × 3/16 in.) packed with 20% SE-30 on Gas-Chrom Q (60–100 mesh), using the internal standard technique. In all cases, each peak was identified by collecting the compound as it eluted from the chromatograph and comparing its infrared spectrum with that of an authentic sample. The per cent yields are based on starting imidoyl chloride.

Reaction of 6-Methylpyrimidine 1-Oxide with *N*-Phenylbenzimidoyl Chloride. 6-Methylpyrimidine 1-oxide (0.70 g, 6.4 mmol) was azeotroped with dry (Na) benzene (10 ml) and then dissolved in chlorobenzene (10 ml). The solution was added dropwise with stirring at room temperature to a solution of *N*-phenylbenzimidoyl chloride (0.71 g, 3.3 mmol) in chlorobenzene (10 ml). It was boiled under reflux for 8 hr, cooled, and concentrated, and the residue was chromatographed on a column of silica gel (100 g) to give benzanilide (0.22 g, 33%); ir (KBr) identical with that of an authentic sample.

The second fraction, eluted with $CHCl_3$, was 2-anilino-4-methylpyrimidine (0.070 g, 11.5%): mp 92–93.5° (ethanol) [lit.[10] mp 92–93°]; ir (KBr) 3250, 3180 cm^{-1} (NH); nmr ($CDCl_3$) δ 8.22 (d, 1 H, $J_{5,6}$ = 5.3 Hz, H-6), 7.62 (d of d, 2 H, J_o = 7.5 Hz, J_m = 1.5 Hz, phenyl-*o*-H), 7.7–7.6 (br s, 1 H, exchangeable with D_2O, N-H), 6.97 (t of d, 1 H, $J_{o,m} = J_{m,p}$ = 7.5 Hz, $J_{o',m}$ = 1.5 Hz, phenyl-*m*-H), 7.27 (t of t, 1 H, $J_{m,p}$ = 7.5 Hz, $J_{o,p}$ = 1.5 Hz, phenyl-*p*-H), 6.52 (d, 1 H, $J_{5,6}$ = 5.3 Hz, H-5), 2.33 (s, 3 H, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 186 (7), 185 (55, $M^{\cdot+}$), 184 (100).

Anal. Calcd for $C_{11}H_{11}N_3$: C, 71.33; H, 5.99. Found: C, 71.09; H, 6.12.

The third fraction consisted mainly of **2-*N*-benzoylanilino-4-methylpyrimidine** (0.14 g, 15%). Crystallization from aqueous ethanol gave the analytical sample (0.012 g, 1.3%): mp 141.5–142°; ir (KBr) 1670 cm^{-1} (C=O); nmr ($CDCl_3$) δ 8.34 (d, 1 H, $J_{5,6}$ = 5 Hz, H-6), 7.6–7.1 (m, 10 H, aromatic-H), 6.80 (d, 1 H, $J_{5,6}$ = 5 Hz, H-5), 2.26 (s, 3 H, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 289 (3, $M^{\cdot+}$), 105 (100).

Anal. Calcd for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.23. Found: C, 74.56; H, 5.30.

Reaction of 4,6-Dimethylpyrimidine 1-Oxide with *N*-Phenylbenzimidoyl Chloride. A solution of 4,6-dimethylpyrimidine 1-oxide (1.04 g, 8.36 mmol) in chlorobenzene (20 ml) was added to freshly prepared and distilled *N*-phenylbenzimidoyl chloride (0.90 g, 4.18 mmol). The solution was boiled under reflux for 10 hr. The solvent was distilled and the black residue was chromatographed on a column of silica gel (100 g). The first fraction eluted (chloroform) was benzanilide (0.24 g, 29%). The second fraction was a mixture containing mainly 2-anilino-4,6-dimethylpyrimidine (0.14 g), mp 71–73°. Fractional crystallization from aqueous ethanol gave benzanilide (0.006 g, 0.7%) and 2-anilino-4,6-dimethylpyrimidine (0.074 g, 9%): mp 91–92° [lit.[11] mp 96–97°]; ir (KBr) 3250 and 3180 cm^{-1}; nmr ($CDCl_3$) δ 7.64 (d of d, 2 H, J_o = 8.0 Hz, J_m = 1.3 Hz, phenyl-*o*-H), 7.24 (m, 3 H, N-H and phenyl-*m*-H), 6.94 (t of t, 1 H, J_o = 7.5 Hz, J_m = 1.3 Hz, phenyl-*p*-H), 6.43 (s, 1 H, H-5), 2.31 (s, 6 H, 4- and 6-CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 199 (3), 198 (6), 197 (24).

The next fraction, also eluted with chloroform, was **2-*N*-benzoylanilino-4,6-dimethylpyrimidine** (0.42 g, 22%): mp 174–175° (aqueous EtOH); ir (KBr) 1670 cm^{-1} (amide C=O); nmr ($CDCl_3$) δ 7.82 (d of d, 2 H, J_o = 7 Hz, J_m = 3 Hz, benzoyl-*o*-H), 7.64–7.36 (m, 8 H, phenyl-H and benzoyl-*m*-and *p*-H), 6.95 (s, 1 H, H-5), 2.27 (s, 6 H, 4- and 6-CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 303 (4, $M^{\cdot+}$), 105 (100).

Anal. Calcd for $C_{19}H_{17}N_3O$: C, 75.22; H, 5.65. Found: C, 75.18; H, 5.81.

Reaction of Pyridazine 1-Oxide with *N*-Phenylbenzonitrilium Hexachloroantimonate. A solution of pyridazine *N*-oxide (1.72 g, 17.7 mmol) in ethylene chloride was added over a period of 10 min to a suspension of *N*-phenylbenzonitrilium hexachloroantimonate (5.25 g, 8.9 mmol) in ethylene chloride (50 ml) (drybox). All the salt dissolved during the addition of the *N*-oxide. The solution was boiled under reflux for 17 hr. After cooling to room temperature, the solution was stirred with water (25 ml) for 10 min to form insoluble antimony compounds and then filtered. The organic layer was dried, concentrated, and chromatographed on a column of silica gel (100 g). Chloroform elution gave benzanilide (0.094 g, 5.3%). Further elution with chloroform gave **3-*N*-benzoylanilinopyridazine** (0.44 g, 18%): mp 149–150° (aqueous acetone); ir (KBr) 1640 cm^{-1} (amide C=O); nmr ($CDCl_3$) δ 8.89 (d of d, 1 H, $J_{5,6}$ = 5 Hz, $J_{4,6}$ = 2 Hz, H-6), 7.65–7.00 (m, 12 H, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 274 (1, $M^+ - 1$), 105 (100).

Anal. Calcd for $C_{17}H_{13}N_3O$: C, 74.16; H, 4.76. Found: C, 74.35; H, 4.92.

1-Benzylbenzimidazole 3-Oxide.[12] *o*-Nitro-*N*-benzylformanilide (20 g, 0.078 mol) was added to ethanol (200 ml) and ethanolic ammonia (100 ml, saturated at 0°). Hydrogen sulfide was passed through the solution which was stirred at room temperature for 2 hr. The mixture was then stirred overnight. The brown solution was concentrated to 100 ml, cooled, and filtered to remove precipitated sulfur. Evaporation of the filtrate, addition of acetone, and chilling gave the crude product (9.45 g). Crystallization from acetone gave 1- benzylbenzimidazole 3-oxide monohydrate (2.0 g, 11.4%): mp 158–159° [lit.[12] mp 47–50° for the trihydrate]; ir (KBr) 1204 (N^+–O^-), 716 cm^{-1} (monosubstituted phenyl); nmr ($CDCl_3$) δ 8.63 (s, 1 H, H-2), 7.94 (m, 1 H, H-4), 7.5–7.1 (m, 8 H, aromatic H), 5.29 (s, 2 H, $PhCH_2$), 3.70 (br s, *ca.* 1.5 H, H_2O of hydrate); mass spectrum (70 eV) *m/e* rel intensity) 224 (2.4), 223 (1.2), 209 (5.6), 208 (10), 119 (1), 92 (11), 91 (100), 90 (5), 77 (7), 73 (9), 71 (5), 69 (6), 65 (19), 63 (9), 57 (9), 55 (9), 51 (7), 44 (22), 43 (10), 41 (12), 40 (44), and 39 (15).

The sample for analysis had mp 78.5–79.5° before drying, mp 161.5–163° after drying for 1 hr at 50° (0.005 mm), and mp 149–151° after drying for 12 hr at 50° (0.005 mm).

Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39. Found: C, 74.96; H, 5.56.

Reaction of 1-Benzylbenzimidazole 3-Oxide with *N*-Phenylbenzimidoyl Chloride. 1-Benzylbenzimidazole 3-oxide (1.21 g, 5.0 mmol) was dried by azeotroping it with chloroform (2 × 10 ml). A solution of *N*-phenylbenzimidoyl chloride (0.54 g, 2.5 mmol) in chloroform (10 ml) was added, and the solution was boiled under reflux for 22 hr. The solution was evaporated to dryness and the residue dissolved in ethanol. Decolorization, addition of water, and seeding gave **2-*N*-benzoylanilino-1-benzylbenzimidazole** (0.90 g, 92%): mp 151.5–153.5° (from EtOH); ir (KBr) 1690 cm^{-1} (amide C=O); nmr ($CDCl_3$) δ 7.64 (m, 1 H, H-4), 7.5–6.9 (m, 18 H, aromatic-H), 5.21 (s, 2 H, Ph CH_2).

Anal. Calcd for $C_{26}H_{21}N_3O$: C, 80.37; H, 5.23; N, 10.42. Found: C, 80.41; H, 5.54; N, 10.37.

2-Anilino-1-benzylbenzimidazole. (a) 2-*N*-Benzoylanilino-1-benzylbenzimidazole (0.029 g, 0.072 mmol) was boiled under reflux in 5% NaOH (3 ml) for 13 hr. After cooling to room temperature,

the solution was filtered and the solid obtained was boiled under reflux with another portion of 5% aqueous NaOH (3 ml) for 48 hr. The solid obtained (0.039 g) consisted mainly of sodium silicate plus the desired compound. It was boiled with chloroform and filtered. The filtrate was evaporated to give 2-anilino-1-benzylbenzimidazole (0.004 g, 18.5%), mp 183–184.5°; ir (KBr) identical with that of sample obtained as under (b) below.

(b) 1-Benzylbenzimidazole 3-oxide (0.242 g, 0.001 mol) was dried by azeotroping it with chloroform (2 × 5 ml) and dissolving in chloroform (3 ml). The solution was stirred at room temperature and phenyl isocyanate (0.12 g, 0.001 mol) was added slowly through a syringe. The reaction mixture set to a solid after the addition was complete. The solid (0.30 g, mp 184.5–189°) was recrystallized twice from chloroform to give **2-anilino-1-benzylbenzimidazole** (0.27 g, 90%): mp 188–190°; ir (KBr) 3200 cm^{-1} (NH); nmr ($CDCl_3$) δ 7.56 (m, 1 H, H-4), 7.40–6.80 (m, 13 H, aromatic-H), 5.14 (s, 2 H, $PhCH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 299 (3, M·+), 207 (6, M − benzyl).

Anal. Calcd for $C_{20}H_{17}N_3 \cdot \frac{1}{2}H_2O$: C, 77.81; H, 5.81; N, 13.62. Found: 77.70; H, 5.75; N, 13.14.

Reaction of Isoquinoline 1-Oxide with *N*-Phenylbenzimidoyl Chloride. Preparative Run. A solution of isoquinoline *N*-oxide (2.08 g, 14.4 mmol) and distilled *N*-phenylbenzimidoyl chloride (2.76 g, 13 mmol) in 1,2-dichloroethane (30 ml) was boiled under reflux for 6 hr. The cooled solution was washed with 10% sodium carbonate solution (2 × 30 ml), the solvent evaporated from the organic phase, and the residue chromatographed on silica gel (250 g, 4 ft × 1.5 in.) using light petroleum–acetone (9:1 v/v) as eluent.

Eluting first was a red oil which was distilled to give 4-chloroisoquinoline (0.33 g, 18%): bp 90° (0.5 mm) [lit.[13] bp 100–104° (1 mm)]; nmr ($CDCl_3$) δ 8.94 (s, 1 H, H-1), 8.43 (s, 1 H, H-3), 8.10–7.28 (m, 4 H, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 165 (31), 164 (10), 163 (100).

The second compound eluted was benzanilide (1.0 g, 39%).

The third product was recrystallized from light petroleum–acetone to give **1-(*N*-benzoylanilino)isoquinoline** (1.6 g, 47%): mp 175–176°; ir (KBr) 1670 cm^{-1} (C=O); nmr ($CDCl_3$) δ 8.24 (d, 1 H, $J_{3,4}$ = 6 Hz, H-3), 8.13 (br d, 1 H, $J_{7,8}$ = 6 Hz, H-8), 7.82–6.94 (m, 14 H, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 324 (8, M·+), 105 (100).

Anal. Calcd for $C_{22}H_{16}N_2O$: C, 81.48; H, 4.94. Found: C, 81.29; H, 5.19.

Analytical Run. A solution of isoquinoline *N*-oxide (3.62 g, 25 mmol) and *N*-phenylbenzimidoyl chloride (5.1814 g) in 1,2-dichloroethane (65 ml) was boiled under reflux for 6 hr. The mixture was cooled to room temperature, then was transferred to a 100-ml volumetric flask and made up to volume with 1,2-dichloroethane. Exactly 4 ml of this solution was added to *n*-octadecane (0.05681 g, 2.24×10^{-4} mol) and the mixture washed with 10% potassium carbonate solution (2 × 5 ml), the aqueous phases were extracted with 1,2-dichloroethane (3 ml), the combined organic phases dried ($CaCl_2$) and analyzed by gas chromatography. The results are given in Table I.

1-(*N*-Benzoylanilino) isoquinoline. A solution of 1-anilinoisoquinoline[14] (1 g, 4.5 mmol) and benzoyl chloride (0.65 g, 4.6 mmol) in dry pyridine (5 ml) was boiled under reflux for 2 hr, poured into water (25 ml), and cooled to 0°. The insoluble crystalline material was filtered, then recrystallized from aqueous ethanol to give 1-(*N*-benzoylanilino) isoquinoline (0.44 g, 30%), mp 175–177°, whose infrared spectrum was indentical with that of the compound obtained as described above.

Reaction of Quinoline 1-Oxide with *N*-Phenylbenzimidoyl Chloride. Preparative Run. (a) A solution of freshly distilled quinoline 1-oxide (2.42 g, 17 mmol) and 1,2-dichloroethane (50 ml) was added to freshly distilled *N*-phenylbenzimidoyl chloride (2.86 g, 13.3 mmol). An immediate exothermic reaction ensued. The mixture was boiled under reflux for 8 hr after which it was cooled and the solvent evaporated *in vacuo*. The residue (*ca.* 5.0 g) was dissolved in chloroform (30 ml), stirred with sodium bicarbonate for 1 hr, then chromatographed on silica gel (500 g) using a mixture of light petroleum–acetone (9:1 v/v) as eluent. Four main products were obtained. Eluting first was benzanilide (0.28 g, 12%).

Eluting second and overlapping slightly with benzanilide was 3-quinolyl benzoate (2.18 g, 33%): mp 59–60° (ethanol); ir (KBr) 1740 cm^{-1} (C=O); nmr ($CDCl_3$) δ 8.81 (d, 1 H, $J_{2,4}$ = 2.5 Hz, H-2), 8.28–8.04 (m, 3 H), 7.99 (d, 1 H, $J_{2,4}$ = 2.5 Hz, H-4), 7.8–7.54 (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 249 (4, M·+), 105 (100); identical with a sample prepared by benzoylation of 3-hydroxyquinoline in pyridine.

Eluting third with slight overlap with 3-quinolyl benzoate was **2-(*N*-benzoylanilino)quinoline** (1.28 g, 30%): mp 116–117° (ethanol); ir (KBr) 1645 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.95 (d, 1 H, $J_{3,4}$ = 9 Hz, H-4), 7.78–6.99 (m, 15 H); mass spectrum (70 eV) *m/e* (rel intensity) 324 (9, M·+), 105 (100).

Anal. Calcd for $C_{22}H_{16}N_2O$: C, 81.48; H, 4.94. Found: C, 81.60; H, 5.27.

The final product to elute was 2-anilinoquinoline (1.96 g, 33%): mp 101–102° (petroleum ether, bp 30–60°) [lit.[15] mp 98°]; ir (KBr) 3420 cm^{-1} (NH); nmr ($CDCl_3$) δ 7. 86–6.90 (m, aromatic protons), 6.82 (d, 1 H, $J_{3,4}$ = 9 Hz, H-3); mass spectrum (70 eV) *m/e* (rel intensity) 221 (8.9), 220 (59, M·+), 219 (100).

As the solvent polarity was increased (increasing the per cent of acetone) traces (<1%) of two other products were isolated. The first was found to be 3-hydroxyquinoline, mp 198–200° [lit.[16] mp 198°]. Its infrared spectrum was identical with that of an authentic sample. The second product was 2-hydroxyquinoline, mp 197–199° [lit.[17] mp 199–200°]. Its infrared spectrum was identical with that of an authentic sample.

(b) A mixture of quinoline 1-oxide (1.27 g, 8.8 mmol), *N*-phenylbenzimidoyl chloride (1.72 g, 8.0 mmol), and 1,2-dichloroethane (15 ml) was boiled under reflux for 6 hr. The solvent was removed *in vacuo*, 6 *N* HCl (10 ml) was added to the residue, and the resulting solution was boiled under reflux for 4 hr. On cooling, benzoic acid (0.69 g, 70%) precipitated. The filtrate was extracted with chloroform (3 × 10 ml). The organic extracts and the aqueous phase were then analyzed separately.

The organic phase was dried ($MgSO_4$), filtered, and the solvent removed. The residue was chromatographed on silica gel (100 g) using a light petroleum–acetone mixture (9:1 v/v) as solvent to yield benzanilide (0.36 g, 23%) and 2-anilinoquinoline (0.91 g, 50%).

The aqueous phase was cooled to 0°, and slowly neutralized with 20% NaOH solution. At pH 7, 3-hydroxyquinoline (0.34 g, 29%), mp 197–200° [lit.[16] mp 198°], precipitated.

3-Quinolyl *N*-Phenylbenzimidate. A solution of 3-hydroxyquinoline[16] (1.10 g, 7.6 mmol) in ethanol (10 ml) and a solution of *N*-phenylbenzimidoyl chloride (1.64 g, 7.6 mmol) in anhydrous ether (5 ml) were added in quick succession to a solution of sodium (0.18 g, 7.8 mmol) in ethanol (50 ml). The solution was stirred at room temperature for 12 hr, then the solvent was removed *in vacuo*. The residual oil was shaken with water (10 ml) and the water decanted. The oil was dissolved in ethanol, boiled with activated charcoal, filtered, and cooled to give **3-quinolyl *N*-phenylbenzimidate** (0.86 g, 35%): mp 114–115°; ir (KBr) 1660 cm^{-1} (C=N); mass spectrum (70eV) *m/e* (rel intensity) 324 (0.6, M·+), 180 (100).

Anal. Calcd for $C_{22}H_{16}N_2O$: C, 81.48; H, 4.94. Found: C, 81.28; H, 5.07.

Attempted Reaction of 3-Quinolyl *N*-Phenylbenzimidate with Quinoline 1-Oxide and Hydrogen Chloride. A solution of 3-quinolyl *N*-phenylbenzimidate (0.041 g, 0.126 mmol) and quinoline 1-oxide (0.055 g, 0.378 mmol) in 1,2-dichloroethane (10 ml) was boiled under reflux for 4 hr. After this period, thin-layer chromatography showed only starting materials to be present. A saturated solution of hydrogen chloride in 1,2-dichloroethane (3 ml) was added and the mixture boiled under reflux for 20 hr. At the end of this time thin-layer chromatography showed that other than starting material a trace amount of a third compound to be present. The mixture was stirred with anhydrous sodium carbonate (3 g) for 1 hr, the filtered solution was concentrated, and the products were separated by preparative thin-layer chromatography on silica gel (25 g, 40 × 20 × 0.085 cm) using pentane–acetone (9:1 v/v) as eluent. Three compounds were isolated after the preparative plate had been developed three times. The compound with highest R_f value was identified by its infrared spectrum as 3-quinolyl *N*-phenylbenzimidate (0.03 g, 75%). The second compound was isolated in such small amounts that only a mass spectrum could be obtained. The mass spectrum of this compound was very similar to that of 2-(*N*-benzoylanilino)quinoline. The final compound isolated was identified by its infrared spectrum as quinoline 1-oxide (0.037 g, 67%). No 2-anilinoquinoline or 3-quinolyl benzoate were detected.

Reaction of Quinoline 1-Oxide with *N*-Phenylbenzimidoyl Chloride. Analytical Run. A solution of quinoline 1-oxide (6.335 g, 44 mmol) in 1,2-dichloroethane (25 ml) was added to *N*-phenylbenzimidoyl chloride (8.5801 g, 40 mmol) in 1,2-dichloroethane (25 ml) and the mixture was boiled under reflux for 6 hr. The solution was cooled to room temperature, the volume was measured and found to be 63.8 ml. Exactly 3 ml of this solution was added to *N*-

(*p*-tolyl)benzamide (0.1238 g, 5.87×10^{-4} mol) (internal standard), the solution was stirred for 3 hr with anhydrous sodium bicarbonate and then analyzed by gas chromatography.

2-(*N*-Benzoylanilino)quinoline. To a solution of 2-anilinoquinoline[15] (0.55 g, 2.5 mmol) in pyridine (3 ml) was added benzoyl chloride (0.36 g, 2.5 mmol) and the mixture boiled under reflux for 1 hr, cooled to room temperature, and water (20 ml) added. The precipitate was filtered and recrystallized from ethanol to give 2-(*N*-benzoylanilino)quinoline (0.53 g, 63%), mp 116–117°.

Reaction of Quinoline 1-Oxide with *N*-Phenylbenzonitrilium Hexachloroantimonate. Preparative Run. To a stirred suspension of *N*-phenylbenzonitrilium hexachloroantimonate (10.30 g, 0.02 mol) in 1,2-dichloroethane (20 ml) was added quinoline 1-oxide (3.2 g, 0.022 mol) in 1,2-dichloroethane (10 ml). An immediate exothermic reaction occurred and the nitrilium salt was consumed. The mixture was stirred at room temperature overnight and poured into a 10% aqueous sodium carbonate, the inorganic salts were filtered, the organic layer was separated, the aqueous solution was extracted with 1,2-dichloroethane (20 ml), and the solvent was evaporated. Half the residue was chromatographed on silica gel (200 g) using light petroleum–acetone (9:1 v/v) as eluent. The first product to elute was a small amount of a solid which, after recrystallization from ethanol, was shown to be *N,N'*-diphenylbenzamidine hydrochloride, mp 285–290° dec [lit.[18] mp 300°]. Its infrared spectrum was identical with that of an authentic sample.

Eluting second was an oil composed of at least two compounds. This oil was dissolved in anhydrous ether and dry hydrogen chloride was bubbled into solution until a precipitate began to form. The mixture was allowed to stand for 2 min then filtered. The precipitate was identified as *N,N'*-diphenylbenzamidine hydrochloride (0.16 g, 5%), mp 285–290° dec by comparison of its infrared spectrum with that of an authentic sample.

The above ether filtrate was washed with 10% sodium carbonate solution (2 × 20 ml), the organic phase was dried ($MgSO_4$) and filtered, and the ether was evaporated. The residue was recrystallized from light petroleum to yield 3-quinolyl benzoate (0.40 g, 16%), mp 59–60°, identical in all respects with an authentic sample.

The final product obtained was benzanilide (0.38 g, 19%).

The second half of the residue obtained from the reaction of quinoline 1-oxide with *N*-phenylbenzonitrilium hexachloroantimonate was added to 6 *N* HCl (10 ml) and boiled under reflux for 6 hr. The mixture was brought to pH 9 with sodium carbonate and extracted with chloroform (3 × 10 ml), the solvent was evaporated, and the residue was chromatographed on silca gel (200 g) using light petroleum–acetone (9:1 v/v) as eluent.

Eluting first was *N,N'*-diphenylbenzamidine (0.19 g, 7%), identified by comparison of its infrared spectrum with that of an authentic sample. The second product to be obtained was 2-anilinoquinoline (0.09 g, 4%), mp 101–102° (light petroleum, bp 30–60°). The final product obtained was 3-hydroxyquinoline (0.2 g, 14%).

Analytical Run. A solution of quinoline 1-oxide (0.638 g, 0.44 mmol) in 1,2-dichloroethane (5 ml) was added to a stirred suspension of *N*-phenylbenzonitrilium hexachloroantimonate (2.183 g, 0.42 mmol) in 1,2-dichloroethane (15 ml) and the resulting mixture was stirred at room temperature for 12 hr. The mixture was poured into 20% sodium carbonate solution (100 ml), the inorganic salts were filtered, the organic phase was separated, and the aqueous phase was washed with 1,2-dichloroethane (10 ml). The combined organic phases were dried ($MgSO_4$), filtered, concentrated to approximately one-half of their original volume, then analyzed by gas chromatography.

Reaction of 4-Nitroquinoline 1-Oxide with *N*-Phenylbenzimidoyl Chloride. A solution of 4-nitroquinoline 1-oxide (4.75 g, 0.025 mol) in 1,2-dichloroethane (30 ml) and *N*-phenylbenzimidoyl chloride (4.27 g, 0.02 mol) in 1,2-dichloroethane (20 ml) was heated under reflux for 6 hr. A portion (20 ml) of this solution (59 ml) was extracted with 10% sodium carbonate (2 × 15 ml), the solvent evaporated, and the residue chromatographed on silica gel (200 g, 4 ft × 1.5 in.) using light petroleum–acetone (9:1 v/v) as eluent. Eluting first was benzanilide (1.15 g, 29%). An oily mixture containing several products was then obtained which could not be solved further by this method. Overlapping somewhat with this mixture was then eluted **4-chloro-3-quinolyl benzoate:** mp 115–116° (benzene–light petroleum); ir (KBr) 3075 (aromatic C-H), 1745 (ester C=O), 1600, 1495, 1450 (aromatic ring stretching), 1255, 1245 (C-O), 1275, 1225, 1215, 1185, 1145, 1140, 1080, 1060, 1025, 935, 915, 820, 755, 705 (monosubstituted aromatic), and 685 cm^{-1}; nmr ($CDCl_3$) δ 8.81 (s, 1 H, H-2), 8.56 (d, 1 H, $J_{7,8}$ = 8 Hz, H-8), 8.30–7.25 (m, 8H, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 285 (0.43), 284 (0.26), 283 (1.2), 181 (0.33), 105 (100).

Anal. Calcd for $C_{16}H_{10}ClNO_2$: C, 67.73; H, 3.55. Found: C, 68.13; H, 3.79.

The final product to elute was 4-chloroquinoline 1-oxide (0.068 g, 2%): mp 132–135° [lit.[19] mp 133–135°]; ir (KBr) 1300 cm^{-1} (N-O); nmr ($CDCl_3$) δ 8.86–8.73 (m, 1 H, H-8), 8.43 (d, 1 H, $J_{2,3}$ = 7 Hz, H-2), 8.25–8.15 (m, 1 H, H-5), 7.92–7.64 (m, 2H, H-6,7), 7.37 (d, 1 H, $J_{2,3}$ = 7 Hz, H-3).

The oily mixture was boiled under reflux for 4 hr with 4 *N* HCl (15 ml), and then basified with sodium carbonate. It was extracted with chloroform (3 × 10 ml), the chloroform was evaporated, and the residue was chromatographed on silica gel (150 g, 3 ft × 1.5 in.) using light petroleum–acetone (9:1 v/v) as eluent. Three products were obtained. Eluting first was 2-anilino-4-chloroquinoline (0.2 g, 4%): mp 161–162° (light petroleum) [lit.[7] mp 161°]; ir (KBr) 3285, 3220, 3180, 3145 cm^{-1} (NH); mass spectrum (70 eV) *m/e* (rel intensity) 256 (11), 255 (51), 254 (77), 253 (100), 252 (19), 219 (19), 218 (23), 217 (6), 216 (6), 190 (6), 165 (4), 164 (4), 163 (4), 162 (8), 128 (13), 127 (21), 126 (17), 115 (11), 114 (11), 110 (4), 109.5 (31), 109 (21), 108.5 (6.4), 101 (13), 100 (8), 99 (8), 96 (6), 95.5 (8), 95 (6), 91 (6), 90 (25), 89 (6), 88 (6), 77 (38), 76 (11), 75 (21), 74 (13), 66 (17), 65 (11), 64 (25), 63 (13), 57 (6), 55 (6), 52 (15), 51 (64), 50 (25), 44 (25), 43 (11), 44 (8), 40 (29), 39 (43), 38 (8), 37 (4), 36 (4).

The second compound to elute was 4-chloro-3-hydroxyquinoline: mp 205–207° (benzene) [lit.[20] mp 206–207°]; ir (KBr) 3150–2500 (br) (bonded OH), 1350, 1230 (OH deformation, C-O stretching), 1150, 835, and 755 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 181 (35), 179 (100), 152 (1.3), 150 (3.4), 143 (8), 115 (53).

Finally 4-chloroquinoline 1-oxide (0.04 g, 1%) eluted. Yields of all the above compounds were not determined accurately; however, with the exception of 4-chloro-3-quinolyl benzoate, all products were obtained in less than 10% yield. The total yield of 4-chloro-3-quinolyl benzoate was approximately 10%.

Reaction of 2,6-Dimethylpyridine 1-Oxide with *N*-Phenylbenzimidoyl Chloride. Preparative Run. A solution of 2,6-dimethylpyridine 1-oxide (2.70 g, 2.20×10^{-2} mol) in 1,2-dichloroethane (30 ml) was added to a solution of freshly distilled *N*-phenylbenzimidoyl chloride (4.2557 g, 1.98×10^{-2} mol) in 1,2-dichloroethane (20 ml) and the mixture heated under reflux for 24 hr. The mixture was cooled to room temperature, transferred to a 100-ml volumetric flask, and made up to volume with 1,2-dichloroethane. The products were isolated by preparative thin-layer chromatography on silica gel (25 g per 40 × 20 × 0.85 cm plate) using light petroleum–acetone (85:15 v/v) as eluent. Each plate was developed five times, then the products were extracted from the silica gel using acetone. Yields obtained from these preparative thin-layer separations were not calculated. Products are described in order, the fastest moving compound (highest R_f value) first, the slowest moving compound last.

The top band was found to be due to 3-chloro-2,6-dimethylpyridine: bp 174–176° [lit.[4] bp 175–176°]; nmr (CCl_4) δ 8.02 (AB quartet, 2 H, $J_{4,5}$ = 8 Hz, H-4,5), 2.46 (s, 3 H, 2-CH_3), 2.36 (s, 3 H, 6-CH_3); identical with an authentic sample.

The second band was due to 2-chloromethyl-6-methylpyridine: bp 90° (30 mm) [lit.[5] bp 81° (12 mm)]; nmr (CCl_4) δ 7.45 (t, 1 H, $J_{3,4} = J_{4,5}$ = 7.8 Hz, H-4), 7.15 (d, 1 H, $J_{3,4}$ = 7.8 Hz, H-3), 6.92 (d, 1 H, $J_{4,5}$ = 7.8 Hz, H-5), 4.51 (s, 2 H, CH_2Cl), 2.43 (s, 3 H, CH_3); identical with an authentic sample.

The component contained in the third band was recrystallized from light petroleum–acetone to give ***O*-3-(2,6-dimethylpyridyl)-*N*-phenylbenzimidate:** mp 129–130°; ir (KBr) 1660 (C=N), 1230 cm^{-1} (C-O); nmr (acetone-d_6) δ 8.00–6.90 (m, 12 H), 2.55 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), mass spectrum (70 eV) *m/e* (rel intensity) 302 (0.53), 182 (1), 181 (16), 180 (100), 152 (1), 105 (4), 78 (4), 77 (50), 76 (2), 57 (1), 53 (4), 52 (2), 51 (17), 50 (3), 43 (1), 42 (2), 41 (1), 39 (2).

Anal. Calcd for $C_{20}H_{18}N_2O$: C, 79.47; H, 5.96. Found: C, 79.31; H, 5.91.

The fourth component was benzanilide.

The sixth component was found to be 2,6-dimethylpyridine 1-oxide.

Quantitative Analysis. A mixture of 2,6-dimethylpyridine 1-oxide (2.70 g, 2.20×10^{-2} mol) and *N*-phenylbenzimidoyl chloride (4.2557 g, 1.98×10^{-2} mol) in 1,2-dichloroethane (50 ml) was boiled under reflux for 24 hr. The mixture was cooled to room temperature, transferred to a 100-ml volumetric flask, and made up to volume with 1,2-dichloroethane. Exactly 5 ml of this solution was added to *n*-octadecane (0.0688 g, 2.71×10^{-4} mol), the mixture was washed with 10% potassium carbonate (2 × 5 ml), the aqueous

phase was extracted with 1,2-dichloroethane (5 ml), and the combined organic phases were dried ($CaCl_2$) and analyzed by gas chromatography. The product yields are given in the Discussion section.

3-(2,6-Dimethylpyridyl)-*N*-phenylbenzimidate. To a solution of sodium ethoxide (0.28 g, 0.0035 mol) in absolute ethanol (10 ml) were added in quick succession 2,6-dimethyl-3-hydroxypyridine (0.43 g, 0.0033 mol) in absolute ethanol (10 ml) and distilled *N*-phenylbenzimidoyl chloride (0.70 g, 0.0033 mol) in dry ether (5 ml). The mixture was allowed to stand for 3 hr at room temperature then filtered through Celite filter-aid. The solvent was evaporated to give a crystalline material. Recrystallization from light petroleum–acetone gave 3-(2,6-dimethylpyridyl)-*N*-phenylbenzimidate (0.75 g, 75%), identical with the compound obtained above.

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Registry No.—**1**, 1613-37-2; **2**, 53112-31-5; **3**, 5468-85-9; **4**, 32888-92-9; **7**, 32888-93-0; **10**, 32953-48-3; **11**, 2405-06-3; **12**, 3099-29-4; **14**, 32888-94-1; **15**, 4637-59-6; **17**, 32888-95-2; *N*-phenylbenzimidoyl chloride, 4903-36-0; *N*-phenylbenzonitrilium hexachloroantimonate, 51293-24-4; *o*-nitro-*N*-benzylformanilide, 53112-32-6; 2-anilino-1-benzylbenzimidazole, 24068-33-5; 1-anilinoisoquinoline, 13797-20-1; 3-hydroxyquinoline, 580-18-7; 4-nitroquinoline 1-oxide, 56-57-5; 4-chloro-3-hydroxyquinoline, 32435-60-2.

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Pyridazino[1,2-*a*]pyridazine Chemistry. An Attempted Synthesis of 1,6-Diazacyclodecapentaene

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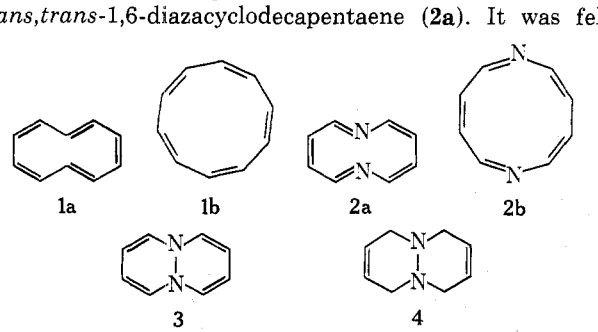
Some new derivatives of the pyridazino[1,2-*a*]pyridazine ring system have been prepared and their chemistry has been studied as possible synthetic precursors to 1,6-diazacyclodecapentaene.

Several years ago it was suggested[1] that the destabilizing effect[2a] of interior nonbonded hydrogen repulsion in *trans,trans*-cyclodecapentaene (**1a**) could be avoided in *trans,trans*-1,6-diazacyclodecapentaene (**2a**). It was felt



1a **1b** **2a** **2b**

3 **4**

that interaction between electron pairs on nitrogen in **2a** might not be serious and therefore the molecule might possibly exist in a nearly strain-free planar configuration. Furthermore, differences in bond angle requirements for the carbon–nitrogen bonds might be sufficient to enable the *all-cis*-1,6-diazacyclodecapentaene (**2b**) to exist as a stable planar species as opposed to the all carbon system **1b**.[2a,b]

The above considerations, as related to obtaining a monocyclic 10π-electron system exhibiting aromatic stability, indicated **2** to be an interesting synthetic objective.

Results and Discussion

Consideration of various synthetic approaches to **2** suggested a "valence-bond"[3] route as an attractive possibility. Accordingly, the synthetic objective was reduced to one of devising a suitable method for the preparation of the unknown pyridazino[1,2-*a*]pyridazine (**3**).

Scrutiny of the literature reveals no known derivatives of ring system **3**; indeed, even saturated derivatives of **3** have been little studied.[4] A reasonable synthetic path appeared to be to prepare a partially saturated derivative of **3** (*e.g.*, **4**) and introduce the additional unsaturation *via* a halogenation–dehydrohalogenation sequence.

The readily available dihydropyridazino[1,2-*a*]pyridazinedione **6**[5] appeared an obvious precursor to **4** if reduction of the hydrazide function to the corresponding hydrazine could be carried out. In practice, this was accom-