3040–2700, 1660, 1440, 1400, 1370, 1335, 1255, 1070, 1105, 1048, 968, 920, 750; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7 Hz, 6 H), 1.52–2.32 (m, 4 H), 2.55–3.18 (m, 6 H), 3.20–3.51 (m, 1 H), 3.81 (d, J = 8 Hz, 1 H); MS, m/e (relative intensity) 205 (M^+, 6), 176 (2), 160 (32), 144 (36), 135 (30), 130 (24), 114 (20), 107 (13), 97 (13), 91 (12), 86 (23), 83 (51), 82 (51), 75 (13), 70 (100); pale yellow oil; $[\alpha]^{23}_D$ -31.8 (c 0.434, $CHCl_3$); 96% yield; TLC, $CHCl_3$ saturated with NH_4OH. Anal. Calcd for $C_9H_{19}NS_2$: 205.0959. Found: 205.0954.

Convergent Coupling Method. The 2-nitrobenzoyl chloride (4.2 mM, 1 equiv, prepared from the corresponding 2-nitrobenzoic acid and oxalyl chloride[8]) was taken up in THF (20 mL) and added dropwise to an ice-cold solution of **20** (4.2 mM, 1 equiv) and triethylamine (8.4 mM, 2 equiv) in THF (30 mL). After addition was completed, the reaction mixture was warmed to room temperature and stirred for an additional 1 h. The mixture was then filtered and evaporated in vacuo, to give an oil that was dissolved in EtOAc (20 mL) and extracted with 0.5 M HCl (4 × 20 mL), saturated $NaHCO_3$ solution (4 × 20 mL), and brine (2 × 10 mL), dried ($MgSO_4$), and evaporated in vacuo to afford the coupled product. By this method, **5a** was countersynthesized in 92% yield; $[\alpha]^{25}_D$ -204.4 (c 0.1712, $CHCl_3$).

Acknowledgment. This work was supported through NIH Grant CA-35318 and by the SmithKline Beckman Corp. Philadelphia. We gratefully acknowledge useful discussions with Drs. Laurence H. Hurley and Steven F. Cheatham of the University of Texas at Austin and Drs. John Hoover and Ken Holden of SmithKline Beckman. Kwongsang Huh is also thanked for preparing intermediate **11**. We are indebted to Dr. Paul Mazzocchi of the University of Maryland for useful discussions and for supplying spectroscopic data on prothracarcin.

Registry No. (*E*)-**2d**, 81542-99-6; (*Z*)-**2d**, 105120-29-4; **3a**, 105089-64-3; **4a**, 72435-94-0; **4b**, 100243-62-7; **4c**, 100230-83-9; **5a**, 105089-65-4; **5b**, 105089-68-7; **5c**, 105089-72-3; **6a**, 105089-66-5; **6b**, 105089-69-8; **6c**, 105089-73-4; **7a**, 105120-27-2; **7a** (11*S* methyl ester), 100230-77-1; **7a** (11*R* methyl ester), 105120-28-3; **7b**, 105089-70-1; **7c**, 105089-74-5; **8a**, 72435-89-3; **8b**, 100231-11-6; **8c**, 100231-12-7; **10**, 552-16-9; (*E*)-**11**, 105089-75-6; (*Z*)-**11**, 105089-76-7; (*E*)-**12**, 105089-77-8; (*Z*)-**12**, 105089-78-9; (*E*)-**13**, 105089-79-0; (*Z*)-**13**, 105089-80-3; (*E*)-**14**, 105089-81-4; (*Z*)-**14**, 105089-82-5; (*E*)-**15**, 105089-83-6; (*Z*)-**15**, 105089-84-7; (*E*)-**16**, 105089-85-8; (*Z*)-**16**, 105089-86-9; **17**, 5211-23-4; **17** (acid), 1148-11-4; **18**, 71461-30-8; **19**, 105089-87-0; **20**, 105089-88-1; *N*-(2-nitrobenzoyl)proline, 18877-33-3; (±)-*N*-(3-methyl-2-nitrobenzoyl)proline, 105089-67-6; (±)-*N*-(5-methyl-2-nitrobenzoyl)proline, 105089-71-2; 2-nitrobenzoyl chloride, 610-14-0.

Reactions of an *o*-Quinone Monoimide with 1,3,5-Trimethoxybenzene, 2-Methoxythiophene, 2-Methoxyfuran, and 1-Methyl-, 2-Methyl-, and 1,2-Dimethylindoles

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Received March 31, 1986

The *o*-quinone monoimide **1** reacts with the electron-rich aromatic reagents 1,3,5-trimethoxybenzene, 2-methoxythiophene, and 1-methyl-, 2-methyl-, and 1,2-dimethylindoles to give the *N*-2,4-dichloro-6-hydroxyphenyl derivatives of *N*-(2,4,6-trimethoxyphenyl)-, *N*-(5-methoxy-2-thienyl)-, *N*-(1-methyl-1*H*-indol-3-yl)-, *N*-(2-methyl-1*H*-indol-3-yl)-, and *N*-(1,2-dimethyl-1*H*-1-indol-3-yl)-4-nitrobenzamides, compounds **8**, **10**, and **19a–c**, respectively. Treatment of **1** with 2-methoxyfuran forms the 2-benzoxazolyl-2-propenoate **14**.

In previous papers we reported that the *o*-quinone monoimide **1** underwent cycloadditions with electron-rich alkenes to form 2,3-dihydro-1,4-benzoxazines **2** (Scheme I).[1,2] More recently we observed that **1** when treated with sulfoxides, diazoalkanes, and triphenylphosphine gave sulfoximines **3**, imines **4**, and the benzoxazole **5**[3] (Scheme I). A rationalization for the latter reactions has the electron-rich sulfur, carbon, and phosphorus atoms of the above reagents bonding to the electron-deficient nitrogen atom of **1** to form the phenoxide ion intermediate **6**. Addition of the phenoxide ion of **6** to the carbonyl carbon forms intermediate **7**, which is the precursor to compounds **3–5**.[3]

An earlier observation that **1** combined with benzofuran to give a cycloadduct, furo[3,2-*b*][1,4]benzoxazine, prompted us to treat **1** with other aromatic substrates, namely, 1-methyl-, 2-methyl-, and 1,2-dimethylindoles, 1,3,5-trimethoxybenzene, 2-methylthiophene, and 2-methoxyfuran. In contrast to benzofuran the products are phenols save in the case of 2-methoxyfuran. An intermediate analogous to **6** is presumed to form in each reaction.

Treatment of **1** with 1,3,5-trimethoxybenzene in methylene chloride gave **8** in 86% yield (Scheme II). Proof of structure rested on an X-ray crystallographic examination of a single crystal of **8**. One plausible mechanistic route to **8** involves attack on the nitrogen of **1** by the electron-rich 1,3,5-trimethoxybenzene to give **9**. Alternatively, a one electron transfer process may take place to give a radical cation and radical anion which can collapse to **9**. Loss of a proton from the benzenium ion moiety of **9** produced **8** (Scheme II). The reaction may be regarded overall as an electrophilic substitution of 1,3,5-trimethoxybenzene by the novel electrophile **1**. No reaction of **1** occurred with anisole under comparable experimental conditions.

2-Methoxythiophene undergoes the same reaction with **1** or with the benzoquinone monoimide **11** to give the

(1) Heine, H. W.; Barchiesi, B. J.; Williams, E. A. *J. Org. Chem.* **1984**, *49*, 2560.
(2) Garbauskas, M. F.; Williams, A. W.; Heine, H. W. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1217.
(3) Heine, H. W.; Empfield, J. R.; Golobish, T. D.; Williams, E. A.; Garbauskus, M. F. *J. Org. Chem.* **1986**, *51*, 829.

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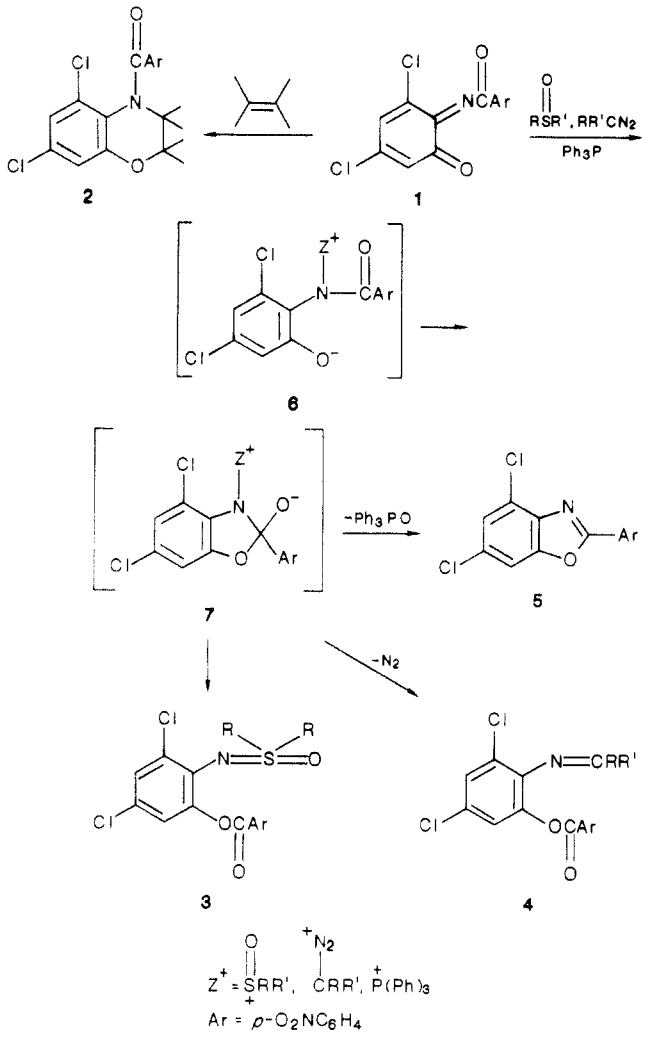
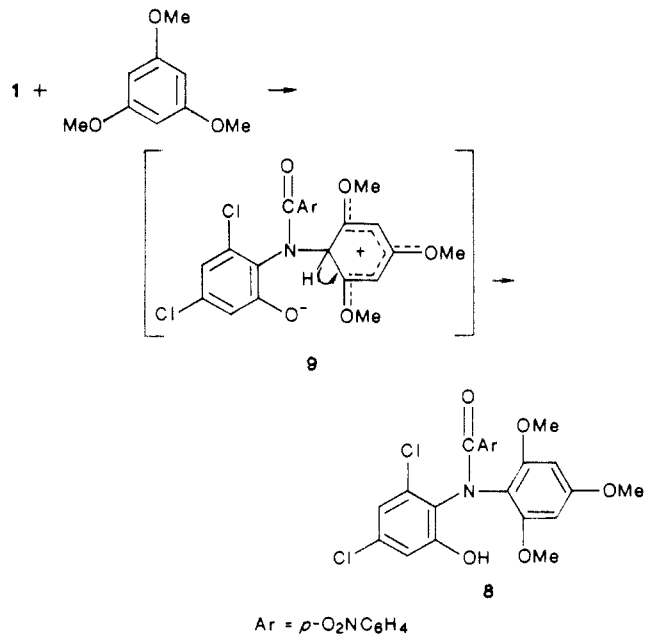
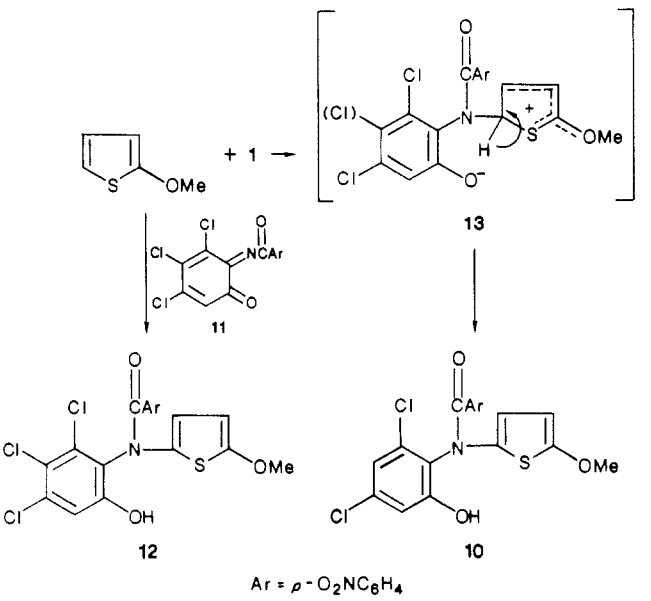
Scheme I



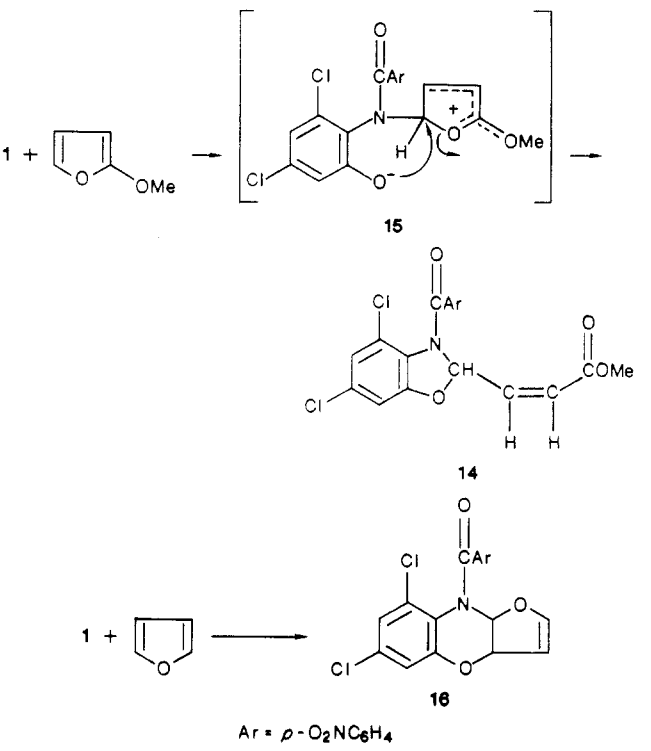
Scheme II



Scheme III



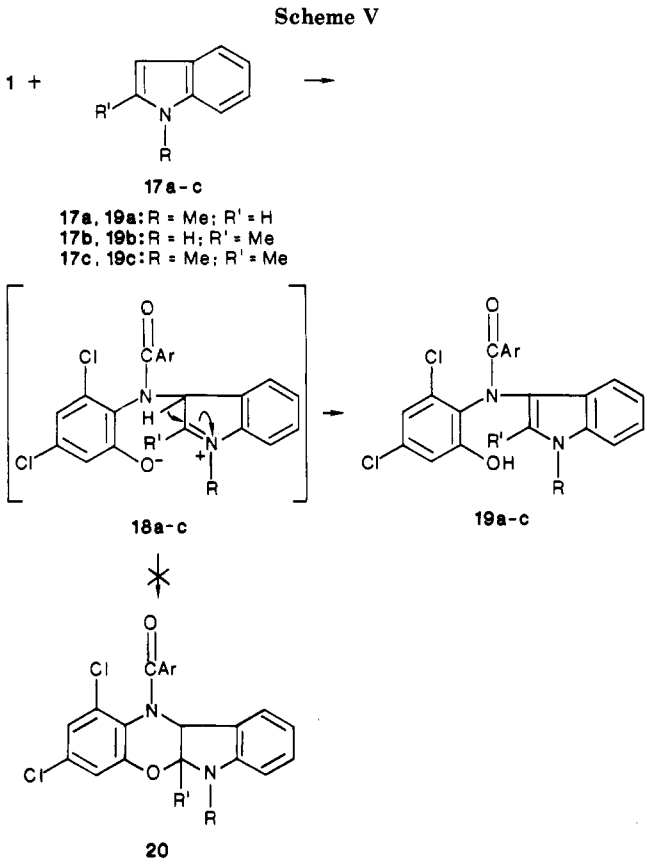
Scheme IV



5-substituted thiophenes **10** and **12** (Scheme III). The structure of **10** was established by X-ray crystallography. Compound **10** crystallized from benzene as a benzene solvate (0.5 mol of benzene to 1 mol of **10**) as calculated from elemental analyses. The problem of the solvate was avoided when 2-methoxythiophene was reacted with **11** to give **12**. Compound **12** crystallized from acetonitrile without complication. The formation of **10** and **12** can be rationalized by presupposing the intermediacy of **13**. Aromatization of the thiophenium ion of **13** yields the phenol **10**.

Reaction of **1** with 2-methoxyfuran produced **14** (Scheme IV), the structure of which was confirmed by X-ray crystallography. Presumably, an intermediate **15** analogous to **9** and **13** is initially formed. The difference in reaction products when **1** was treated with 2-methoxythiophene and 2-methoxyfuran may be a consequence of the relative abilities of sulfur and oxygen atoms to stabilize the positive charges of intermediates **13** and **15**. The 3p orbitals of sulfur overlap less efficiently with the aromatic π system of **13** than do the corresponding 2p orbitals of oxygen in

Scheme V



15. The better overlap in **15** renders the oxygen bonded to the methine carbon a good leaving group thereby paving the way for the generation of the ester **14** by an internal S_N2 process. The less effective overlap of the sulfur in **13** and possibly larger contribution to the resonance hybrid by the methoxide oxygen in **13** enhances the acidity of the methine hydrogen resulting in the formation of the phenol **10**. Reaction of **1** with furan itself produces the cycloadduct **16** (Scheme IV).[1]

1-Methyl-, 2-methyl-, and 1,2-dimethylindoles (**17a–c**) combined with **1** to yield the phenols **19a–c** probably via intermediates **18a–c** (Scheme V). The proof of structure of **19a–c** rested on ^{13}C NMR spectroscopy. The ^{13}C NMR data for **19a** and **14** are given in the Experimental Section.

The chemical shift assignments for the *p*-nitrobenzoyl moiety and the phenolic rings were made by comparison of the observed shifts with values calculated from known substituent effects on aromatic rings.[4] Since the spectra were obtained with continuous proton decoupling, carbon atoms with protons directly attached were of greater intensity due to the nuclear Overhauser effect (NOE).[4] The ortho and meta carbon atoms in the *p*-nitrobenzoyl ring were easily identified since there were two of each, and therefore the resonances arising from these carbons were twice the intensity of the other unsubstituted carbons.

The chemical shifts of each corresponding carbon in the phenolic rings in **19a–c**, **8**, and **10** were within 1–2 ppm of each other. Confirmation of this ring structure was obtained in the crystal structures of **8** and **10**. In contrast, the chemical shifts observed for the chlorinated ring of **14** were quite different (4–6 ppm for C-3 and C-6) than the analogous carbon resonances in the phenolic products. Furthermore, a low-field aliphatic resonance at 90.3 ppm, corresponding to the carbon substituted with nitrogen and

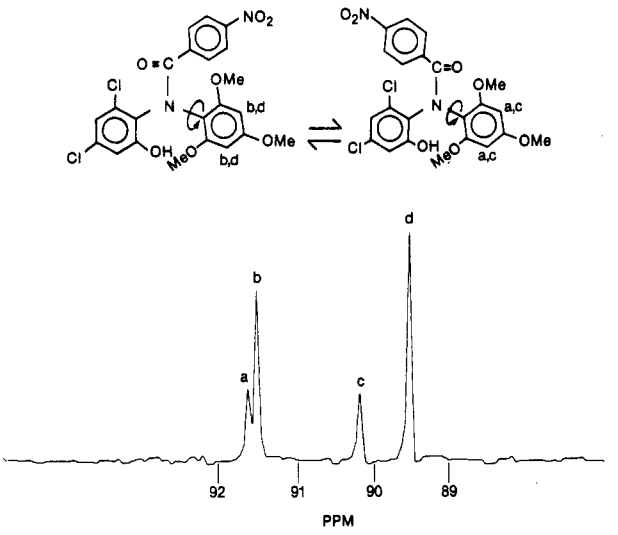


Figure 1. Portion of the carbon-13 NMR spectrum of **8** corresponding to the protonated aromatic carbon atoms of the trimethoxybenzene ring. Major isomer is assumed to have carbonyl syn to the chlorinated aromatic ring as was found in the crystal structure.

oxygen, was observed in **14**. An APT experiment[5] was performed to confirm that this resonance arose from a methine (CH) carbon atom.

Comparison of the chemical shifts in the adducts with the starting electron-rich aromatics showed that the aromatic ring systems remained intact in these adducts. Confirmation that the substitution occurred at the C-3 carbon of the indole came from the disappearance of the protonated carbon resonance arising from C-3 in the starting indoles (99–102 ppm) and the appearance of a new resonance at lower field (~114 to ~115 ppm) in the adducts. The new resonance had the characteristic lower intensity of a fully substituted carbon atom.

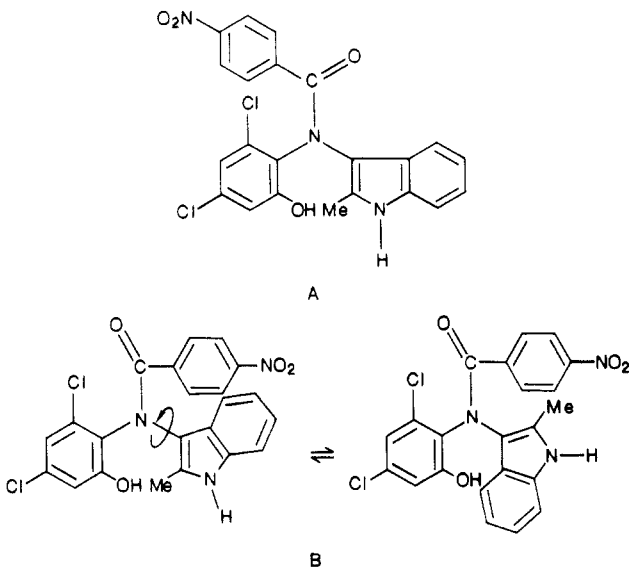
The ^{13}C NMR spectra of **8**, **10**, and **19a–c** at −30 °C showed isomers arising from slow rotation about the amide nitrogen–carbonyl bond which coalesced to single peaks for each carbon at higher temperatures. Compounds **8** and **19b,c** showed additional resonances which we have attributed to restricted rotation about the nitrogen–aryl bond of the trimethoxybenzene ring of **8** and the indole rings of **19b,c**. The barriers to rotation must be fairly high since complete coalescence of the resonances required temperatures greater than 140 °C for all three compounds. Restricted rotation about the nitrogen–aryl bonds in **8** arises from steric crowding of the two ortho methoxy groups. The region of the ^{13}C spectrum at −30 °C which corresponds to the unsubstituted carbon atom on the trimethoxybenzene ring of **8** is shown in Figure 1. The four peaks observed are assumed to arise from the two distinct carbons on either side of the aryl ring, with one pair of peaks for each amide isomer. The major isomer probably has the carbonyl group syn to the chlorinated aromatic ring as was found in the crystal structure. At about 140 °C the four peaks coalesce to a broad singlet. Similar high barriers to rotation about nitrogen–aryl bonds in anilides and related compounds have been reported.[6] The assumption that two ortho substituents are required to inhibit rotation

(4) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972.

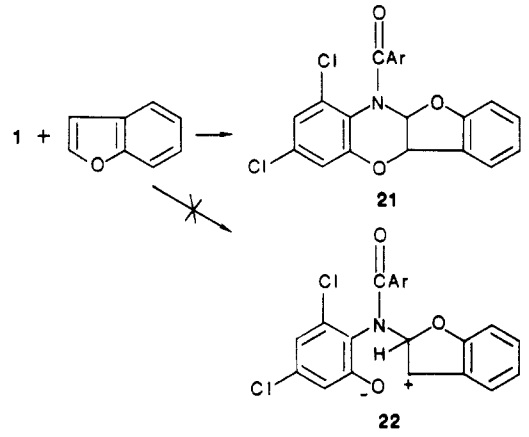
(5) Patt, S. L.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 435.

(6) (a) Stewart, W. E.; Siddall, T. H. *Chem. Rev.* **1970**, *70*, 517. (b) Sternhell S. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975; pp 163–201. (c) *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Wilen, S. H., Eds.; Interscience Publication: New York 1983; Vol. 14, pp 1–81.

Scheme VI



Scheme VII



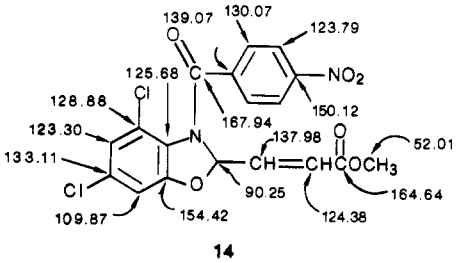
is supported by the observation that **19a** shows only amide isomers, whereas **19b,c** exhibit restricted rotation as evidenced by additional resonances in the ^{13}C spectra. Apparently the additional steric effect of the 2-methyl substituent is necessary since both **19b,c** have this substituent which is absent in **19a**.

Examination of the ^{13}C NMR spectrum of **19b** shows three resonances for most of the carbon atoms in the molecule. It is possible that one of the amide isomers (A) exhibits free rotation about the nitrogen–aryl bond, while for amide isomer (B) two rotational isomers are observed (Scheme VI). Alternatively, one of the four conformers may be sterically unfavorable and present only in very low concentration.

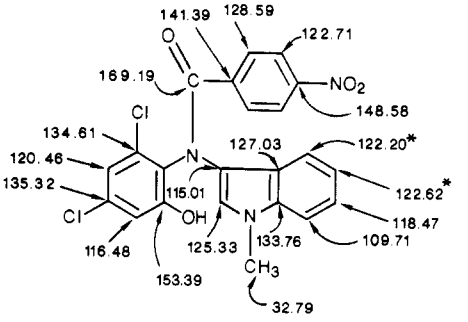
The bonding of the 3-carbon of indole to the electrophilic nitrogen of **1** follows the usually observed substitution pattern of indoles with electrophiles. Presumably the involvement of the basic nitrogen lone pair in the stabilization of the intermediate **18** diminishes the positive charge at the carbon α to the nitrogen so that cyclization to **20** is not as preferred as the loss of a proton from C-3 to give the phenol **19** (Scheme V). In contrast, **1** reacts with benzofuran to form **21** (Scheme VII). The electron-rich C-2 of the benzofuran bonds to the nitrogen of **1** but in this instance it is doubtful that an intermediate similar to **18**, namely **22**, is formed. The benzofuran oxygen of **22** is not in position to stabilize the positive charge at C-3 except through the disruption of the aromatic ring. If **22** is not an intermediate, the formation of the phenol is precluded. It appears more probable that a concerted mechanism is operative in the formation of **21**.

Experimental Section

NMR Measurements. Carbon-13 NMR spectra were obtained on a Varian XL-300 spectrometer operating at 75.4 MHz for ^{13}C. Typical spectral parameters included a 20 kHz spectral width, 32K data points, 12-μs pulse width (corresponding to a 45° flip angle) and 1–3-s pulse delay. The carbon-13 chemical shifts for **14** and **19a** are shown. The values observed for the chlorinated



14



19a

*may be revered

ring and *p*-nitrobenzoyl moiety of **19a** are representative of those obtained for all the phenolic products. The shifts reported for **14** were obtained in $CDCl_3$ at −30 °C. No amide isomers were observed for this compound even at lower temperatures. The data for **19a** were acquired in 1,1,2,2-tetrachloroethane-d_2 at 110 °C to equilibrate the amide isomers.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-4-nitro-*N*-(2,4,6-trimethoxyphenyl)benzamide (8).** To a solution of 532 mg (1.64 mmol) of **1** in 6.0 mL of CH_2Cl_2 was added 276 mg (1.64 mmol) of 1,3,5-trimethoxybenzene. After 4 days at ambient temperature the solvent was evaporated to give 694 mg (86%) of crude **8**. Crystals for X-ray analysis and for elemental analyses were grown by dissolving **8** in a small quantity of CH_2Cl_2 in a beaker and adding just enough *p*-xylene to cause turbidity. Compound **8** can also be recrystallized directly from *p*-xylene, mp 174–176 °C.

Anal. Calcd for $C_{22}H_{18}Cl_2N_2O_7$: C, 53.56; H, 3.68; N, 5.68. Found: C, 53.45; H, 3.96; N, 5.48.

The *p*-nitrobenzoate of **8** was prepared in 66% yield by adding 40 mg of *p*-nitrobenzoyl chloride to a suspension of 105 mg of **8** in 14 mL of Et_2O containing 28 mg of Et_3N. The suspension was stirred for 20 min and was filtered. The solid residue was slurried with H_2O and refiltered. The *p*-nitrobenzoate was purified by dissolution in a small quantity of CH_2Cl_2 and precipitating with mesitylene, mp 256–258 °C.

Anal. Calcd for $C_{29}H_{21}Cl_2N_3O_{10}$: C, 54.22; H, 3.29; N, 6.54. Found: C, 54.46; H, 3.59; N, 6.56.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(5-methoxy-2-thienyl)-4-nitrobenzamide (10).** To a stirred solution of 103 mg (0.90 mmol) of 2-methoxythiophene in 4.0 mL of CH_2Cl_2 was added 283 mg (0.87 mmol) of **1** in portions. The reaction was slightly exothermic. The reaction mixture was allowed to stand 64 h, and then the solvent was evaporated. The orange-brown residue was slurried with MeOH and was filtered to give 337 mg (88%) of crude **10**, mp 75–95 °C. Three recrystallizations from a 3:1 mixture of methylene chloride/toluene gave yellow-orange crystals, mp 96–98 °C; molecular ion, *m/e* 438. An elemental analyses of the crystals indicated a solvate had formed (1 mol of **10** to 0.5 mol of CH_2Cl_2). Recrystallization of **10** from benzene

also gave a solvate, mp 76–80 °C.

Anal. Calcd for $C_{18}H_{12}Cl_2N_2O_5S \cdot {}^1/_2C_6H_6$: C, 52.74; H, 3.16; N, 5.85. Found: C, 52.60; H, 3.30; N, 5.57.

***N*-(2,3,4-Trichloro-6-hydroxyphenyl)-*N*-(5-methoxy-2-thienyl)-4-nitrobenzamide (12).** Compound 11 (115 mg, 0.32 mmol) was added to a solution of 37 mg (0.32 mmol) of 2-methoxythiophene in 1.07 g of CH_2Cl_2. The reaction mixture was allowed to stand for 4 days at ambient temperature, and the solvent was evaporated. The residue was slurried with a small quantity of MeOH and the slurry was filtered to give 120 mg (80%) of 12. Two recrystallizations from CH_3CN afforded 12, mp 207–209 °C.

Anal. Calcd for $C_{18}H_{11}Cl_3N_2O_5S$: C, 45.64; H, 2.34; N, 5.92. Found: C, 45.62; H, 2.30; N, 5.88.

(*Z*)-Methyl 3-[4,6-Dichloro-2,3-dihydro-3-(4-nitrobenzoyl)-2-benzoxazolyl]-2-propenate (14). Compound 1 (315 mg, 0.96 mmol) was added in portions to a solution of 94 mg (0.96 mmol) of 2-methoxyfuran in 2.5 g of $CHCl_3$. The reaction mixture was allowed to stand 1.5 h, and the solvent was evaporated. The residue was triturated with MeOH, and the MeOH was evaporated. The crude 14 weighed 390 mg (96%) and melted at 145–155 °C with decomposition. Recrystallization from acetonitrile gave 14, mp 177–180 °C.

Anal. Calcd for $C_{18}H_{12}Cl_2N_2O_6$: C, 51.08; H, 2.86; N, 6.62. Found: C, 51.08; H, 2.92; N, 6.58.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(1-methyl-1*H*-indol-3-yl)-4-nitrobenzamide (19a).** A mixture of 89 mg (0.68 mmol) of 1-methylindole, 1.6 mL of CH_2Cl_2, and 220 mg (0.68 mmol) of 1 was allowed to stand at ambient temperature for 1 day. The reaction mixture was filtered to give 256 mg (83%) of 19a. A similar reaction with benzene as a solvent gave a precipitate of 19a immediately on admixing. The yield was 82%. Recrystallization from CH_3CN gave 19a, mp 248–250 °C.

Anal. Calcd for $C_{22}H_{15}Cl_2N_3O_4$: C, 57.90; H, 3.31; N, 9.21. Found: C, 57.47; H, 3.37; N, 9.13.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(2-methyl-1*H*-indol-3-yl)-4-nitrobenzamide (19b).** An instantaneous reaction took place when 325 mg (1 mmol) of 1 was added to a solution of 131 mg (1 mmol) of 2-methylindole. The reaction mixture turned black, and then an orange precipitate of 19b formed, which when filtered weighed 425 mg (93%), mp 269–273 °C. Dissolution of 19b in hot MeOH, cooling, and addition of water to turbidity gave 19b, which darkens slightly at 265 °C and decomposed at 274–276 °C.

Anal. Calcd for $C_{22}H_{15}Cl_2N_3O_4$: C, 57.90; H, 3.31; N, 9.21. Found: C, 57.80; H, 3.27; N, 9.15.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(1,2-dimethyl-1*H*-indol-3-yl)-4-nitrobenzamide (19c).** Compound 1 (163 mg, 0.50 mmol) was added in small portions to a solution of 73 mg (0.50 mmol) of 1,2-dimethylindole. The surface of 1 turned black as it was added to the solution. Stirring caused immediate dissolution, and the reaction mixture turned light yellow. After a short time (3–5 min) a precipitate formed. The reaction mixture was filtered after it stood for 8 h. The yield of crude 19c was 222 mg (94%). It was recrystallized twice from CH_3CN to give 19c, mp 255–256 °C dec, with slight discoloration occurring at 248 °C.

Anal. Calcd for $C_{23}H_{17}Cl_2N_3O_4$: C, 58.74; H, 3.64. Found: C, 58.63; H, 3.97.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for Grant CHE-84058555. We thank Dr. Mary F. Garbauskas and Carolyn Hejna for the X-ray crystallographic studies on compounds 8, 10, and 14 and Ashraf Chatterjee and Kim Shepherd for the initial work on 1-methyl- and 1,2-dimethylindoles. We also thank Dr. Robert W. White, Senior Advisor, Chemical Abstracts for checking the nomenclature of compounds.

Supplementary Material Available: Crystal structure data and ORTEP drawings for 8, 10, and 14 (16 pages). Ordering information is given on any current masthead page.

Bridgehead Hydrazines. 4. Oxidative and Basic Ring Cleavage of Pyrazolo- and *s*-Triazolo[1,2-*a*]pyridazines

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Received April 18, 1986

Selenium dioxide oxidation of 2,2-diethyl-5,8-dihydro-5,8-diphenylpyrazolo[1,2-*a*]pyridazine-1,3-dione (6) resulted in oxidative cleavage of the pyrazole ring. Treatment of 6 and of its *s*-triazolo analogue 5 with lithium diisopropylamide resulted in cleavage of the pyridazine ring and formation of 1-hydrazinobutadiene derivatives. Reasons for the instability of the bicyclic systems are discussed. 2,5,8-Triphenyl-*s*-triazolo[1,2-*a*]pyridazine-1,3-dione was prepared from 5 by allylic bromination and basic dehydrobromination.

Available results[1-3] on the photolysis of 1,2-diacyl-1,2-dihydropropyridazines are highly diversified, as any alteration in the structure caused a complete change in the course of the photolysis. However, one trend can be detected, exhibited by the two pairs **1a–1b**[1,2] and **2a–2b**.[3,4] The unsubstituted derivatives **1a** and **2a** behave mainly as dienic 4π systems, and their photoreactions do not involve the nitrogens. The diphenyl derivatives **1b** and **2b**, on the other hand, behave as cyclic 6π systems, and their exclusive initial photoreaction is a conrotatory electrocyclic opening with cleavage of the nitrogen–nitrogen bond. The photolysis of **3a**[3] also fits this pattern, and we were therefore interested in the complementary **3b**. This paper describes some observations made during the synthesis of compound **3b**.

The reported preparation of **1b**[5] involves selenium dioxide oxidation of the corresponding tetrahydro derivative **4**. Accordingly we tried the oxidation of **5** and **6** under the same conditions. The reaction of **5** resulted in decompo-

(1) Altman, L. J.; Semmelhack, M. F.; Hornby, R. B.; Vedenas, J. C. *Chem. Commun.* **1968**, 686.
(2) Rigaudy, J.; Breliere, J. C. *Bull. Soc. Chim. Fr.* **1968**, 455.
(3) Sheradsky, T.; Moshenberg, R. *J. Org. Chem.* **1985**, *50*, 5604.
(4) Sheradsky, T.; Moshenberg, R. *J. Org. Chem.*, in press.
(5) Alder, K.; Niklas, H. *Justus Liebigs Ann. Chem.* **1954**, *585*, 81.

0022-3263/87/1952-0101$01.50/0