THE REACTIONS OF o-QUINONE MONOIMIDES WITH SOME THIOPHENES AND FURANS*

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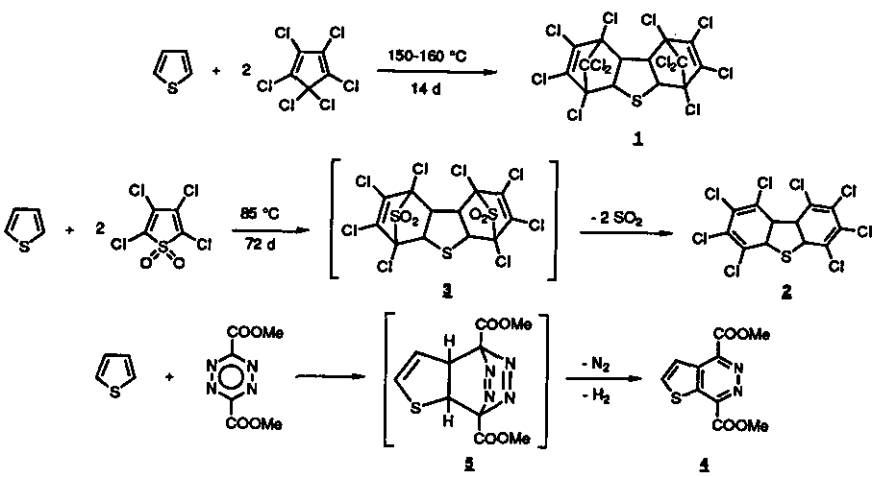
Abstract - o-Quinone monoimides undergo inverse electron demand Diels-Alder reactions with thiophene, 2-alkylated thiophenes, 2- and 2,5- alkylated furans and benzofurans. 2,5-Dimethylthiophenes and 2-methylbenzo[b]thiophene, on the other hand interact with o-quinone monoimides to yield ethers, products arising from hydride abstractions from the methyl groups by the imido nitrogen of **6** .

There are only a few examples of thiophenes or benzo[b]thiophenes acting as the dienophilic component in inverse electron-demand Diels-Alder reactions. Thiophene itself combines with hexachlorocyclopentadiene[1] and tetrachlorothiophene-1,1-dioxide[2] to give compounds (**1**) and (**2**) respectively (Scheme 1). It is presumed that **2** forms by the extrusion of sulfur dioxide from the Diels-Alder intermediate (**3**). Reactions of thiophene and substituted thiophenes with 1,2,4,5-tetrazine-3,6-dimethyldicarboxylate lead to **4** .[3a,b] Compound (**4**) is supposedly formed via the intermediacy of **5** from which, under the reaction conditions employed, nitrogen and hydrogen are lost yielding the aromatic system (**4**). A similar reaction occurs between 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine and benzo[b]thiophene.[4]

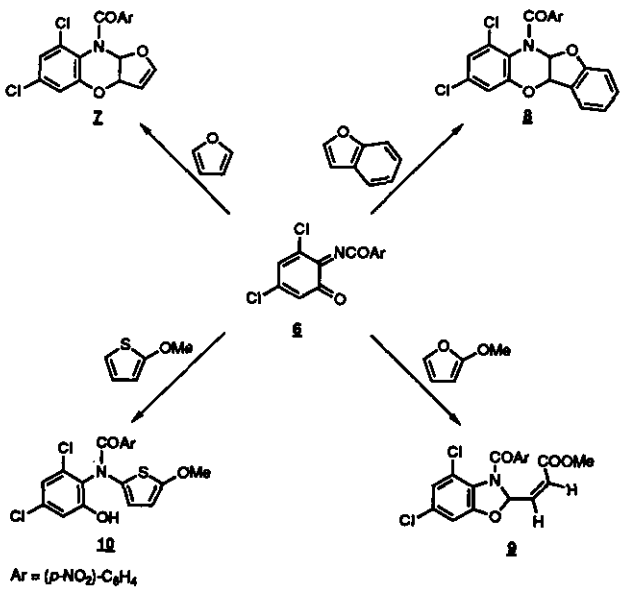
* Dedicated to Professor Edward C. Taylor on the occasion of his 70th Birthday.

Scheme 1



In this paper are reported the reactions of the o-quinone monoimide (**6**) with some thiophenes, benzo[b]thiophenes, furans and benzofurans. We had observed previously that the heterodiene moiety of **6** added to the ene component of furan and benzofuran to form the cycloadducts (**7**) and (**8**)[5] (Scheme 2). Compound (**6**) reacts similarly with

Scheme 2

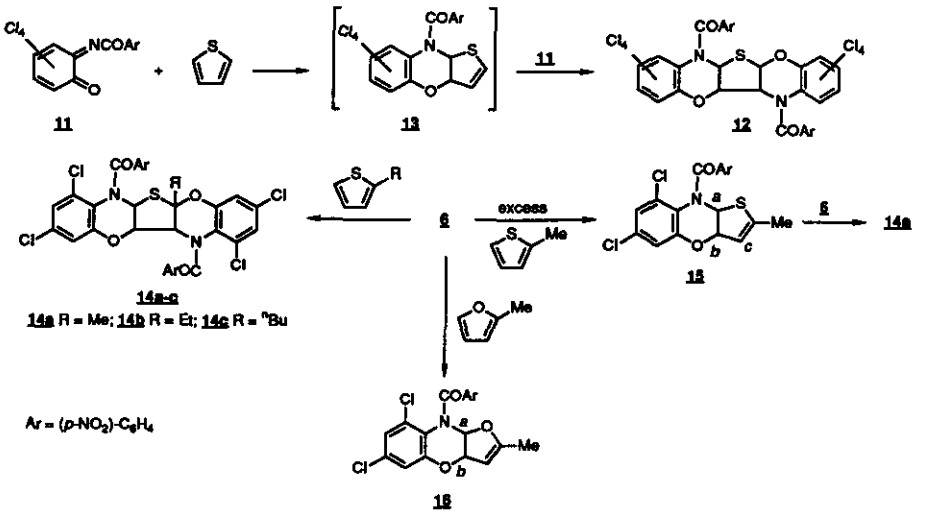


more complex furans such as visnagin and 8-methoxypsoralen.[6] We had also noted that **6** added in a different manner to 2-methoxyfuran and 2-methoxythiophene and formed not cycloadducts but instead compounds (**9**) and (**10**)[7] (Scheme 2).

RESULTS AND DISCUSSION

No reactions occurred when a solution of **6** in thiophene was kept at ambient temperature for thirty days. In contrast (**6**) when added to the less aromatic furan gave the adduct (**7**) within 15 minutes in 99% yield.[5] Thiophene did undergo reaction, however, with the more electrophilic tetrachloro-o-quinone monoimide (**11**) forming the bis adduct (**12**) (Scheme 3) in 90% yield after nine days reaction time. Presumably a 1:1 adduct (**13**) was formed initially but **13**, being a vinyl sulfide, reacted rapidly with additional (**11**) to form **12**. 2-Methyl-, 2-ethyl- and 2-n-butylthiophenes also underwent cyclization with **6** within 18-48 h producing the 2:1 adducts (**14a-c**) (Scheme 3) in high yields. By reacting **6** with a thirteen fold excess of 2-methylthiophene the 1:1 adduct (**15**) was isolated, which when reacted with additional **6** formed the bis adduct (**14a**). The structures of **14a-c** were established by ^{13}C nmr spectroscopy

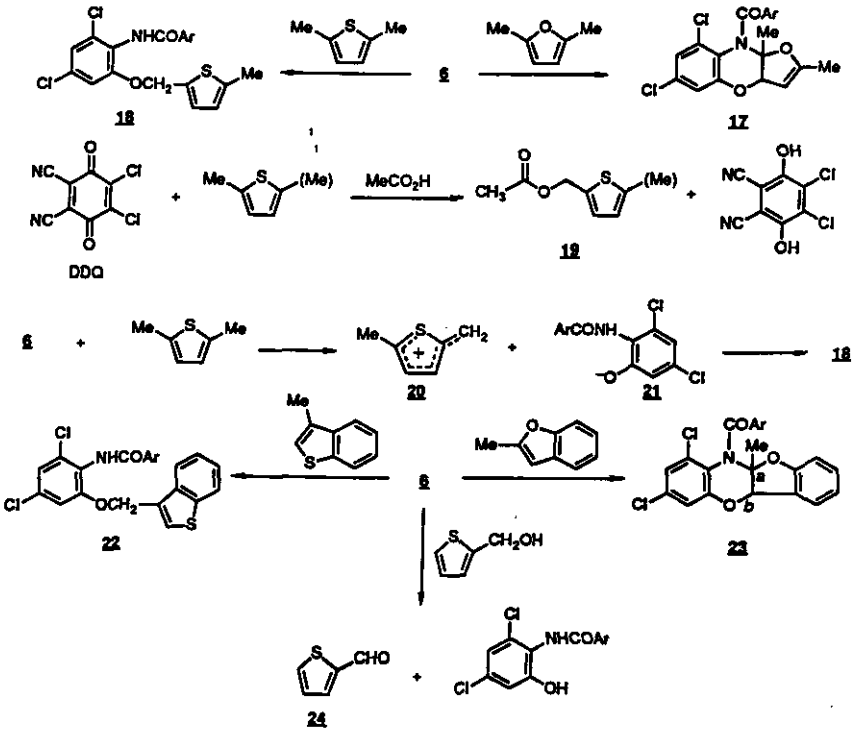
Scheme 3



and in the case of **15** by 2D nmr. Structural assignment of **14c** was based on X-ray crystallography (Figure 1). The ring systems inherent in compounds (**14a-c**) and (**15**) have heretofore not been reported. While the reaction of 2-methylthiophene with **6** took several hours the cycloaddition of 2-methylfuran and **6** formed the mono adduct (**16**), instantaneously.

The ease with which furan and 2-methylfuran undergo inverse electron-demand Diels-Alder reactions relative to thiophene and 2-methylthiophene can be attributed to the greater aromaticity of thiophene which results in an attendant reduction in dienophilicity. This difference in aromaticity between the two heterocyclic systems is further exemplified by comparing the products obtained when **6** is reacted with 2,5-dimethylfuran and 2,5-dimethylthiophene. In the former case the Diels-Alder adduct (**17**) is formed but, in the latter case the ether (**18**) is produced wherein the thiophene ring remains intact (Scheme 4). In a similar reaction 2,3-dichloro-5,6-dicyano-p-benzoquinone

Scheme 4



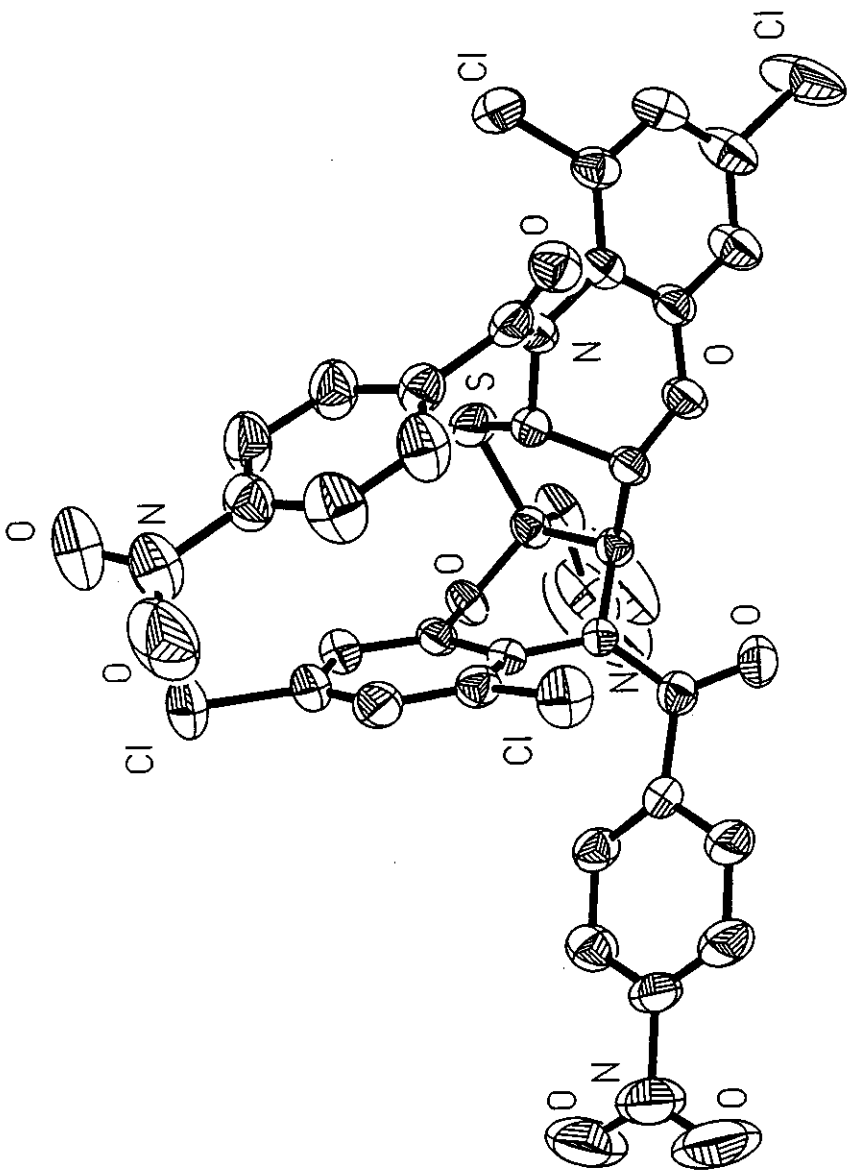


Figure 1. Thermal-Ellipsoid (50% probability) Plot of **14c**

(DDQ) reacts with both 2-methyl- and 2,5-dimethylthiophenes in acetic acid at reflux temperature yielding the corresponding acetates (**19**) (Scheme 4).[8] It was proposed that a hydride ion transfer from a methyl group to DDQ took place producing a carbocation intermediate which subsequently interacted with acetic acid to yield **19**. A hydride ion abstraction can also be envisaged for the reaction of **6** with 2,5-dimethylthiophene. The carbocation (**20**) thus engendered combines with the simultaneously generated anion (**21**) forming **18** (Scheme 4).

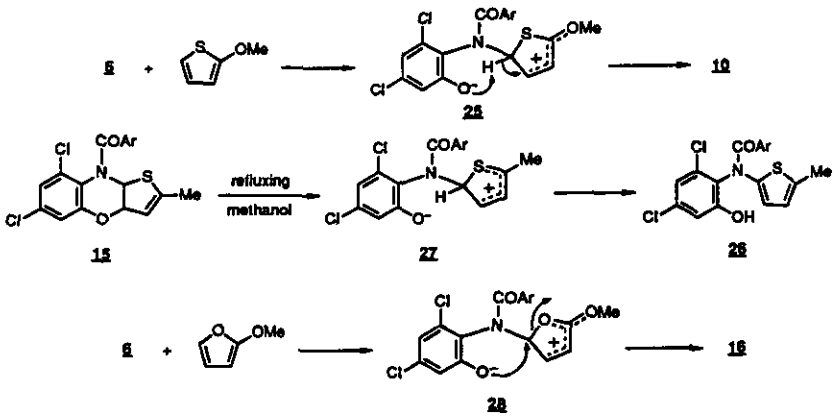
The decreased dienophilicity of thiophenes relative to furans extends to their benzo analogs. Thus a mixture of **6** and benzo[b]thiophene in methylene chloride for several weeks gave no product while **6** and benzofuran formed the cycloadduct (**8**) in one hour (Scheme 2). Compound (**6**) did react, however, with 3-methylbenz[b]thiophene to produce the ether (**22**) (Scheme 4). Under the same conditions **6** and 2-methylbenzofuran yielded the cycloadduct (**23**). The penchant of **6** to form ethers with methylated aromatics has been shown to extend to substrates like hexamethylbenzene and 9,10-dimethylanthracene.[9] We have also observed that **6** reacts with 2-hydroxymethylthiophene, most probably *via* a hydride ion abstraction, producing aldehyde (**24**).

That reaction of **6** and 2-methoxythiophene does not lead to a Diels-Alder adduct but instead to compound (**10**) (Scheme 2) may be ascribed to the formation of a zwitterionic intermediate (**25**) (Scheme 5). The positive charge on the thiophene ring of **25** is effectively delocalized especially by the 2-methoxy group. Conceivably **25** could undergo cyclization to form a Diels-Alder adduct but greater stability is achieved by rearomatization of the thiophene ring through the loss of a proton to the phenoxy anion of **25**. In the reaction of **6** with 2-methylthiophene to give **15** the formation of a zwitterion is not as likely (given that a methyl group lacks the efficacy of a methoxy group to delocalize charge) and a classical inverse electron demand Diels-Alder reaction occurs. Any electron demand that begins to be generated on the thiophene ring as its C-5 atom bonds to the nitrogen of **6** is offset concurrently by the oxygen

of **6** bonding to the C-4 atom of the thiophene ring.

It is interesting to note that the refluxing of **15** *in methanol produces* **26** an analog of **10** . A reasonable rationalization for the transformation is that (**15**) *is converted to the zwitterion* (**27**), *which like* **25** , *loses a proton to the phenoxy* anion to yield **26** (Scheme 5). The structure of **26** was proved by X-ray crystallography and by the preparation of a 2,4-dinitrophenyl ether.

Scheme 5

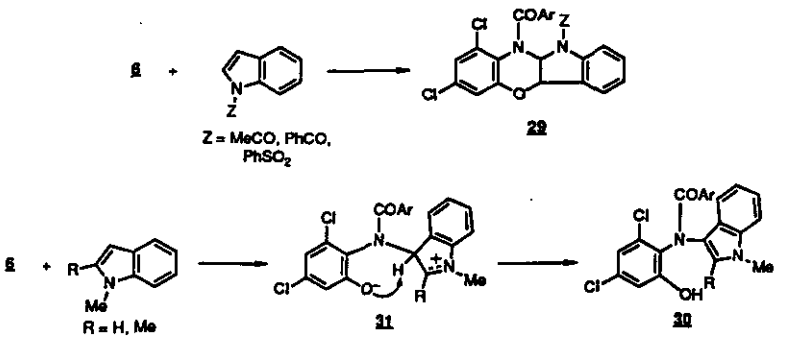


The reactions of **6** with 2-methylfuran and 2-methoxyfuran are similar to those of **6** with the corresponding thiophenes. Thus, **6** and 2-methylfuran undergo cycloaddition to give the Diels-Alder adduct (**16**) (Scheme 3) whilst **6** and 2-methoxyfuran do not yield a cycloadduct but instead the α,β-unsaturated ester (**9**) (Scheme 2). In the latter reaction, it is the supposition that the intermediate is the zwitterion (**28**), the oxygen analog of **25** (Scheme 5). A priori the zwitterion (**28**) could ring close to a Diels-Alder product but instead the phenoxy anion executes an S_N2 attack on the C-5 carbon of the furan thereby generating the stable α,β-unsaturated ester (**16**).

Other heterocyclic systems undergo reactions with **6** that parallel the reactions of **6** with thiophenes and furans. For instance, the Diels-Alder adducts (**29**) are obtained when 1-acyl-, and 1-phenylsulfonylindoles and **6** interact.[10] However, compound (**30**) is produced when **6** is combined with 1-methyl- and 1,2-dimethylindoles[7] (Scheme 6). An explanation for these results is that the 1-methyl- and 1,2-dimethyl-

indoles induce the formation of the zwitterion (31) in which the positive charge on the indole moiety is extensively delocalized by the N-methyl group. This reaction corresponds to that of **6** with 2-methoxythiophene to form **10**. The 1-acyl- and 2-sulfonylindoles, on the other hand, lacking the charge stabilizing ability of the methylated indoles, undergo a synchronous cycloaddition to form **29**.

Scheme 6

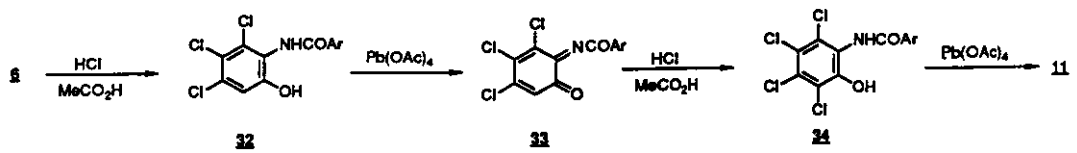


SUMMARY

In summary thiophene and 2-alkylated thiophenes undergo inverse electron demand Diels-Alder reactions with o-quinone monoimides albeit much slower than the corresponding furans. Thiophenes such as 2,5-dimethylthiophene and 3-methylbenzo[b]thiophene interact with o-quinone monoimides via a formal hydride abstraction from the methyl group by the imido nitrogen of the o-quinone monoimide. The generated anion and carbocation subsequently combine to produce the ethers (18) and (22), respectively. 2,5-Dimethylfuran, on the other hand, combines with the o-quinone monoimide to form an inverse electron demand Diels-Alder adduct. 2-Methoxythiophene and 2-methoxyfuran differ from their 2-alkylated analogs by reacting with o-quinone monoimides to form, presumably through the intermediacy of zwitterions, adducts that are more stable than those resulting from Diels-Alder cyclizations.

The o-quinone monoimides (11) and (33) have not been characterized heretofore. They were prepared by the sequence depicted in Scheme 7.

Scheme 7

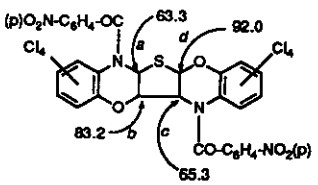


32 33 34

The structure of **32** was established by the reaction of 2-amino-3,4,5-trichlorophenol with p-nitrobenzoylchloride.

EXPERIMENTAL

1,2,3,4,8,9,10,11-Octachloro-5a,6a,12a,12b-tetrahydro-7,13-bis(4-nitrobenzoyl)-7*H*,13*H*-thieno[2,3-*b*:4,5-*b*']bis[1,4]benzoxazine(**12**). To a mixture of 87 mg (0.2 mmol) of **11** and 2.55 ml of CH_2Cl_2 was added 485 mg (5.77 mmol) of thiophene. The solvent was removed after 6 days and the residue triturated with MeOH and the methanol was evaporated. This procedure was repeated five times. The yield of **12** was 94 mg (97%), mp 270-272°C. Compound (**12**) was slurried in hot MeOH and the slurry filtered to give **12** , mp 272-273°C; ms m/z 868/870. Anal. Calcd for $C_{30}H_{12}N_4O_8Cl_8S$: C, 41.31; H, 1.39; N, 6.42. Found: C, 41.61; H, 1.17; N, 6.38. The natural abundance ^{13}C nmr spectrum of **12** ($C_2D_2Cl_4$ at 140°C) is summarized in the following structure:



The spectrum was obtained at elevated temperature to equilibrate amide isomers observed at room temperature.

1,3,8,10-Tetrachloro-5a,6a,12a,12b-tetrahydro-5a-methyl-7,13-bis(4-nitrobenzoyl)-7*H*,13*H*-thieno[2,3-*b*:4,5-*b*']bis[1,4]benzoxazine (**14a**). To a mixture of 112 mg (1.14 mmol) of 2-methylthiophene in 3.92 ml of CH_2Cl_2 was added 371 mg (1.14 mmol) of **6** . After 3 days at ambient temperature the solvent was evaporated and the residue triturated

with EtOH and the EtOH evaporated. The triturations were repeated several times. The crude yield of **14a** was 421 mg (quantitative). Three recrystallizations from MeCN gave **14a** , mp 255-257°C; ms m/z 746/748. Anal. Calcd for $C_{31}H_{18}N_4O_8Cl_4S$: C, 49.75; H, 2.42; N, 7.49. Found: C, 49.72; N, 2.81; N, 7.21; ^{13}C nmr ($CDCl_3$ at 30°C) δ 60.9(65.0)(a), 67.2(70.8)(c), 81.8(84.5)(b), 99.4(105.0) and 29.6 ppm corresponding to the four bridgehead carbons and the methyl carbon. Carbon assignments are shown for **12** . Two resonances were observed for most carbons due to amide isomers which exchanged slowly at low temperature. The chemical shift for the minor isomer is shown in parentheses. In all cases heating the sample to 140°C resulted in rapid equilibration of the isomers and the observation of single peaks for each carbon.

1,3,8,10-Tetrachloro-5a,6a,12a,12b-tetrahydro-5a-ethyl-7,13-bis(4-nitrobenzoyl)-7*H*,13*H*-thieno[2,3-*b*:4,5-*b*']bis[1,4]benzoxazine (**14b**). Compound (**6**) (162 mg, 0.50 mmol) was added to a solution of 56 mg (0.50 mmol) of 2-ethylthiophene in 3.15 ml of ethanol free chloroform. The solvent was evaporated after 3 days and MeOH was added to the gummy residue. This mixture was slurried with a spatula and the MeOH evaporated. Additional MeOH was added and evaporated several times. The yield of **14b** , was 178 mg (93%). Recrystallization from acetone gave **14b** , mp 247-248°C; ms m/z 760/762. Anal. Calcd for $C_{32}H_{20}N_4O_8Cl_4S$: C, 50.42; H, 2.64; N, 7.35. Found: C, 50.30; H, 2.80; N, 7.05; ^{13}C nmr ($CDCl_3$) δ 60.8(64.1)(a), 66.0(69.3)(c), 81.9(85.0)(b) and 104.3-(109.9)(d), 35.1 and 9.30 ppm for the bridgehead carbons; and for the methylene and methyl carbon atoms.

1,3,8,10-Tetrachloro-5a,6a,12a,12b-tetrahydro-5a-n-butyl-7,13-bis(4-nitrobenzoyl)-7*H*,13*H*-thieno[2,3-*b*:4,5-*b*']bis[1,4]benzoxazine (**14c**). A mixture of 63.2 mg (0.45 mmol) of 2-n-butylthiophene, 146 mg (0.45 mmol) of **6** and 2.30 ml of CH_2Cl_2 was kept at ambient temperature for 36 h. The solvent was evaporated and MeOH added to the resinous residue. The white solid that formed was filtered to give 165 mg (92%) of crude (**14c**). Several recrystallizations from MeCN formed **14c** , mp 226-228°C. Anal. Calcd for $C_{34}H_{20}N_4O_8Cl_4S$: C, 51.66; H, 3.06; N, 7.09. Found: C, 51.57; H, 3.66;

N, 7.02; ^{13}C nmr ($CDCl_3$) δ 64.0(60.3)(a), 81.7(84.9)(b), 69.3(66.1)(c) and 109.1-(103.1)(d) for the bridgehead carbons. Carbon assignments are as shown for (12). Chemical shifts for the minor isomer are shown in parentheses. An X-ray crystallographic study by Professor M. Kastner, Bucknell University will be published independently.

6,8-Dichloro-3a,9a-dihydro-2-methyl-9-(4-nitrobenzoyl)-9*H*-thieno[3,2-*b*][1,4]benzoxazine (15). To a solution of 744 mg (7.59 mmol) of 2-methylthiophene in 2.15 ml of CH_2Cl_2 was added 108 mg (0.333 mmol) of **6**. The reaction mixture turned dark red upon the addition of **6** but changed to a light gold color within a few hours. After 18 h the solvent was evaporated. Methanol was added to the residue and the MeOH evaporated. This procedure was repeated five times to give 139 mg (98%) of crude **15**, mp 137-142°C. Recrystallization from acetone gave **15**, mp 147-154°C; ms m/z 425. Anal. Calcd for $C_{18}H_{12}N_2O_4Cl_{12}S$: C, 51.39; H, 3.18; N, 6.49. Found: C, 51.07: H, 2.89; N, 6.61. ^{13}C nmr ($C_2D_2Cl_4$ at 140°C) δ at 65.1(a), 91.0(b) and 115.0(c) ppm; ^1H nmr δ at 7.1(a), 6.1(b) and 5.2(c) ppm. Assignments are for atoms labelled in Scheme 3. The structure of this adduct was determined using homonuclear and heteronuclear correlation spectroscopies. The aliphatic carbon atoms adjacent to nitrogen and oxygen, and the vinyl carbon of the thiophene adduct were identified by their chemical shifts. Heteronuclear correlation spectroscopy identified the protons that correlated with these carbon resonances. Homonuclear correlation spectroscopy and proton decoupling experiments showed that H_a was coupled only to H_b, that H_b was coupled to H_a and H_c, and that H_c was coupled to both the methyl protons and H_a. Based on this information the adduct was identified to be shown in Scheme 3.

6,8-Dichloro-3a,9a-dihydro-2-methyl-9-(4-nitrobenzoyl)-9*H*-furo[3,2-*b*][1,4]benzoxazine (16). To 54 mg (0.66 mmol) of 2-methylfuran in 2.65 ml of CH_2Cl_2 was added dropwise 214 mg (0.66 mol) of **6**. The orange color of **6** was discharged immediately and the reaction mixture became warm. After 5 min the solvent was evaporated. This procedure was repeated two more times twice. The crude **16** weighed 261 mg (97%) and

melted 131-136°C. Recrystallization from MeCN gave **16** , mp. 149-150°C; ms m/z 406. Anal. Calcd for $C_{18}H_{12}N_2O_5Cl_2$: C, 53.09; H, 2.97; N, 6.88. Found: C, 52.98; H, 3.24; N, 6.99, ^{13}C nmr ($CDCl_3$) δ at 95.60(a) and 87.16(b) ppm corresponding to the carbon atoms labelled in Scheme 3.

6,8-Dichloro-3a,9a-dihydro-2,10-dimethyl-9-(4-nitrobenzoyl)-9*H*-furo[3,2-*b*][1,4]benzoxazine (17). To a solution of 64 mg (0.67 mmol) of 2,5-dimethylfuran in 2.50 ml of CH_2Cl_2 was added gradually 216 mg (0.67 mmol) of **6** . The orange color of (6) was discharged immediately upon its addition and the reaction mixture became warm. The solvent was evaporated and the residue slurried several times with MeOH and the methanol evaporated. The crude **17** (268 mg, 95%) melted at 118-125°C. An analytical sample was prepared by dissolving **17** in MeCN at ambient temperature. Addition of water to the solution precipitated **17** . The procedure was repeated to give **17** , mp 142-144°C; ms m/z 420. Anal. Calcd for $C_{19}H_{14}N_2O_5Cl_2$: C, 54.17; H, 3.34; N, 6.65. Found: C, 54.07; H, 3.69; N, 6.54; ^{13}C nmr ($CDCl_3$) δ 17.24 (CH_3), 93.8(a) and 94.4(b). Assignments are shown in Scheme 4.

6,8-Dichloro-3a,9a-dihydro-2,10-dimethyl-9-(4-nitrobenzoyl)-9*H*-thieno[3,2-*b*][1,4]benzoxazine (18). To a stirred solution of 112 mg (1.0 mmol) of 2,5-dimethylthiophene in 3.70 ml of CH_2Cl_2 was added 324 mg (1.0 mmol) of **6** . After seven days at ambient temperature the solvent was evaporated. The residue was slurried with MeOH several times and the MeOH evaporated. The crude **18** (414 mg, 95%, mp 132-144°C) was recrystallized three times from MeCN to give **18** , mp 167-169°C; ms m/z 436. Anal. Calcd for $C_{19}H_{14}N_2O_4Cl_2S$: C, 52.18; H, 3.23; N, 6.41. Found: C, 52.06; H, 3.82; N, 6.36; ^1H nmr ($CDCl_3$) δ 2.38 (S, 3H), 5.20 (S, 2H); ^{13}C nmr, 15.11 (CH_3), 67.8 (CH_3), 164.1 (-CONH).

N-[2-(Benzo[*b*]thien-3-ylmethoxy)-4,6-dichlorophenyl]-4-nitrobenzamide (22). A solution of 81 mg (0.55 mmol) of 3-methylbenz[b]thiophene and 171 mg (0.55 mmol) of **6** in 4.00 ml of CH_2Cl_2 stood at ambient temperature for 7 days. The CH_2Cl_2 was evaporated and the crude **22** (228 mg, 90%, mp 210-216°C) was purified by dissolution in DMSO

followed by precipitation by the addition of H_2O. Filtration afforded **22** (191 mg, 76%, *mp* 228-232°C); *ms* m/z 472; Anal. Calcd for $C_{22}H_{13}N_2O_4Cl_2S$: C, 55.82; H, 2.98; N, 5.92. Found: C, 55.38; H, 2.79; N, 6.02; ^1H nmr ($CDCl_3$) δ 5.32 (S, 2H); ^{13}C nmr, 65.77 (OCH_2), 163.99 (-CONH).

7,9-Dichloro-5a,11a-dihydro-5a-methyl-6-(4-nitrobenzoyl)-6*H*[1]benzofuro[3,2-*b*][1,4]benzoxazine (**23**). A mixture of 62 mg (0.47 mmol) of 2-methylbenzofuran, 152 mg (0.47 mmol) of **6** and 1.65 ml of CH_2Cl_2 stood for 6 days at ambient temperature. The CH_2Cl_2 was evaporated and the red gummy residue slurried three times with MeOH. Evaporation of the MeOH gave a quantitative yield of crude **23** as a tan powder, mp 155-165°C. The crude **23** was dissolved in a minimum of hot MeOH. The solution was cooled and water added to turbidity. Filtration gave **23** (174 mg, 81%, mp 172-174°C) as a white powder. Ms m/z 456; Anal. Calcd for $C_{22}H_{14}N_2O_5Cl_2$: C, 57.58; H, 3.08; N, 6.12. Found: C, 57.82; H, 3.33; N, 6.08; ^{13}C nmr ($CDCl_3$) δ 24.05(CH_3), 90.52(b) and 101.5(a).

2-Thiophenecarboxaldehyde (**24**). To a solution of 47 mg (0.41 mmol) of 2-hydroxymethylthiophene in 1.13 ml of CH_2Cl_2 was added 133 mg (0.41 mmol) of **6**. Within 1 h a precipitate formed. After 2 days at ambient temperature the precipitate was filtered to give 105 mg (78%) of reduced **6** (mp 204-206°C). To the filtrate was added 10 ml of 2,4-dinitrophenylhydrazine solution. The crude 2,4-dinitrophenylhydrazone of 2-thiophenecarboxaldehyde (**24**) was filtered and washed with warm MeCN. The melting point of the 2,4-dinitrophenylhydrazone was 228-231°C; lit., 229-231°C.[11]

Conversion of **15** into **26**. A solution of 55 mg of **15** in 2 ml of MeOH was refluxed for 4 h. Evaporation of the solvent gave 53 mg of crude **26**, mp 113-125°C. A preliminary X-ray crystallographic examination of **26** by Professor Margaret Kastner indicates the structure of **26** as depicted. It was difficult to purify **26**. A 2,4-dinitrophenylether of **26** was prepared which melted at 177-178°C after recrystallization from EtOH; ms m/z 558. Anal. Calcd for $C_{24}H_{14}N_4O_8Cl_2S$. C, 48.91; H, 2.39; N, 9.50. Found: C, 48.52; H, 2.30; N, 9.11.

N-(2,3,4-Trichloro-6-hydroxyphenyl)-4-nitrobenzamide (32). Method A: To a stirred solution of 325 mg (1 mmol) of **6** in 10 ml of glacial HOAc was added 2 ml (24 mmol) of conc HCl. The suspension that formed was stirred for 0.5 h and then 40 ml of ice water added to the mixture. Filtration gave 350 mg of **32**. Recrystallization from EtOH/H_2O (2:1) afforded 295 mg (82%) of **32**, mp 209-211°C; ms m/z 360 which was used directly for the preparation of **33**.

Method B: To a stirred solution of 1 g (4.7 mmol) of 2-amino-3,4,5-trichlorophenol and 1.0 g (9.88 mmol) of Et_3N in 250 ml of anhydrous ether was added dropwise a solution of 925 mg (4.9 mmol) of *p*-nitrobenzoyl chloride in 75 ml of ether. The reaction mixture was stirred for 3.5 h and the creamy suspension containing **32**, Et_3N and some *O*-(2-amino-3,4,5-trichlorophenyl)-4-nitrobenzoate was filtered and the filtrate saved. The solid mixture was washed with two 50 ml portions of ether and the washings combined with the filtrate. Evaporation of the ether gave 350 mg of **32** which, when recrystallized from EtOH/H_2O (2:1) gave **32**, mp 208-211°C. The **32**'s produced by methods A and B were identical.

N-(2,3,4-Trichloro-6-oxo-2,4-cyclohexadien-1-ylidene)-4-nitrobenzamide (33). One mmol (443 mg) of $Pb(OAc)_4$ was added in one portion to a stirred solution of 360 mg (0.99 mmol) of **32** in 100 ml of dry $CHCl_3$. The orange reaction mixture was stirred 15 min and filtered over a two inch bed of Celite. The Celite was washed with 20 ml of $CHCl_3$ and the combined filtrate and washing evaporated. The crude **33** (300 mg, 85%) was recrystallized from MeCN to give **33**, mp 180-181°C (decomp.) Anal. Calcd for $C_{13}H_5N_2O_4Cl_3$: C, 43.42; H, 1.40; N, 7.79. Found: C, 43.31; H, 1.89; N, 7.72.

N-(2,3,4,5-Tetrachloro-6-hydroxyphenyl)-4-nitrobenzamide (34). Concentrated hydrochloric acid (3 ml) was added to a stirred solution of **33** (358 mg, 0.99 mmol) in 10 ml of glacial HOAc. After 2.5 h 75 ml of ice-water was added to the suspension. Filtration gave 360 mg (90%) of crude **34**. The crude **34** was recrystallized from toluene to give **34**, mp 226-228°C. Anal. Calcd for $C_{13}H_6N_2O_4Cl_4$: C, 39.43; H, 1.53; N, 7.07. Found: C, 29.97; H, 1.47; N, 7.12.

N-(2,3,4,5-Tetrachloro-6-oxo-2,4-cyclohexadien-1-ylidene)-4-nitrobenzamide (**11**). Lead tetraacetate (443 mg, 1 mmol) was added in one portion to a stirred solution of 394 mg (1 mmol) of **34** in 150 ml of dry $CHCl_3$. After 15 min the orange solution was filtered over a two inch bed of Celite and the filtrate saved. The Celite was washed with an additional 25 ml of $CHCl_3$. Evaporation of the filtrate and washings produced 325 mg (83%) of crude **11** . Recrystallization from MeCN formed **11** , mp 211-213°C. Anal. Calcd for $C_{13}H_4N_2O_4Cl_4$: C, 36.63; H, 1.02; N, 7.11. Found: C, 39.75; H, 1.09; N, 7.03.

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