Cyclisation of Benzils

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Treatment of several substituted benzils [3,3'- and 4,4'-dimethyl-; 2,2'-, 3,3'- and 4,4'-dichloro-; 3,3'-dibromo-; 4-(*N,N*-dimethylamino)-] with an excess of chlorosulfonic acid gave the corresponding 3-chloro-2-phenylbenzofuran disulfonyl dichlorides. Disubstitution was confirmed by microanalytical and spectral data for the corresponding bis(*N,N*-dimethylaminsulfonamides). The positions of electrophilic substitution were not confirmed with 3,3'-dimethyl-, 2,2'- and 3,3'-dichlorobenzils. With 4,4'-dichlorobenzil, a smaller amount of chlorosulfonic acid enabled the isolation of 3,6,4'-trichloro-2-phenylbenzofuran-5-sulfonyl chloride, which was identified by X-ray analysis of the *N,N*-dimethylsulfonamide. The cyclisation failed with 3,3'-dimethoxy-, and 3,3'- and 4,4'-dinitrobenzils. The results have been interpreted mechanistically.

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The work described in this paper forms part of our general program concerned with the chemistry and biological activity of aromatic sulfonyl derivatives [1-5], and extends previous studies on heterocyclic derivatives [5-7].

We have proposed a mechanism for the reaction of benzil with chlorosulfonic acid in which cyclisation to the benzofuran ring system occurred prior to sulfonation [8]. However, this reaction mechanism now appears to be unlikely. Treatment of the proposed intermediates, 3-chloro-2-phenylbenzofuran and 2-phenylbenzofuran-3-ol [9], with an excess of chlorosulfonic acid (6 molar equivalents) at 40°, conditions identical to those used with benzil, gave mixtures of products. The presence of a carbonyl group was demonstrated in each case, which suggests that the benzofuran ring undergoes degradation. Similar treatment of 2-phenylbenzofuran [10] also confirmed that this compound was not an intermediate in the reaction sequence.

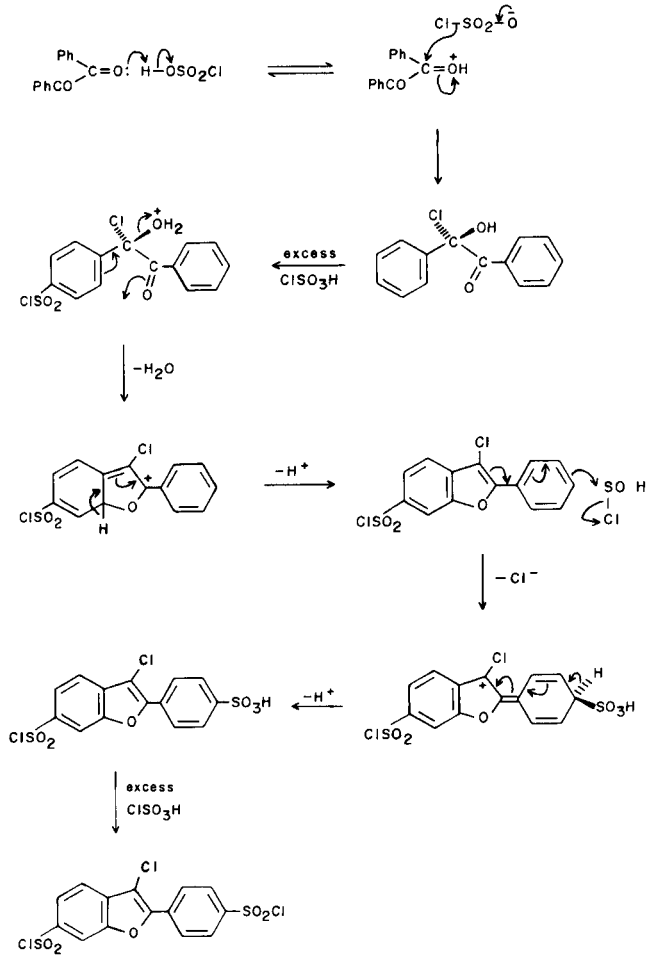
The benzil cyclisation may proceed *via* radical formation. We treated a radical inhibitor, 2,6-di-*t*-butyl-4-cresol, with chlorosulfonic acid. Decomposition occurred, and it was therefore not possible to draw any conclusions from the reaction of benzil and chlorosulfonic acid in the presence of inhibitor.

In the presence of iodine, chlorosulfonic acid is known [11] to chlorinate aromatic substrates by a radical mechanism. We repeated the reaction of benzil with chlorosulfonic acid in the presence of iodine. The product, which could not be identified, contained a carbonyl group, indicating that cyclisation had not occurred. This result suggests that cyclisation is probably not a radical process.

On the basis of the above evidence, an alternative reaction sequence is clearly required. Although a free radical pathway cannot be definitely ruled out, it does appear to be unlikely. We now suggest an alternative route (Scheme 1), which involves the formation of a chlorohydrin intermediate. This significantly reduces the deactivation of the phenyl ring towards electrophilic attack, and allows sulfonation prior to ring-closure. Formation of the benzofuran is facilitated by the presence of a suitable leaving group, and may be influenced by the electron-withdrawing character of the chlorosulfonyl substituent.

Scheme 1

Mechanism for the Cyclisation of Benzil to 3-Chloro-2-phenylbenzofuran-6,4'-disulfonyl Dichloride



In order to test this proposal, and to examine the generality of the reaction, we have treated a monosubstituted and several symmetrically disubstituted benzils with chlorosulfonic acid. Support for the mechanism has been obtained particularly from the chlorosulfonation of 4,4′-dichlorobenzil and 4-(*N,N*-dimethylamino)benzil.

When 4,4′-dichlorobenzil was heated with chlorosulfonic acid (5 molar equivalents), followed by the reaction of the crude sulfonyl chloride with dimethylamine, a dimethylsulfonamide was obtained, and was identified as 3,6,4′-trichloro-2-phenylbenzofuran-5-(*N,N*-dimethylsulfonamide) (Ia), on the basis of microanalytical data and X-ray crystallography. Electrophilic substitution *ortho* to the chlorine atom would be expected, and the product Ia obtained after ring-closure. The presence of the *para*-disubstituted benzene ring was confirmed by the well-defined AA′BB′ pattern in the pmr spectrum. The 4- and 7-protons appeared as a single resonance, and were therefore, under the conditions of the determination, chemically equivalent. A number of other derivatives were prepared (Ib-If).

In the case of 4-(*N,N*-dimethylamino)benzil, treatment with a large excess of chlorosulfonic acid (12 molar equivalents), followed by reaction of the crude product with dimethylamine, gave a bis(*N,N*-dimethylsulfonamide), which was shown to be 3-chloro-4′-(*N,N*-dimethylamino)-2-phenylbenzofuran-4,6-bis(*N,N*-dimethylsulfonamide) (II). There was a two-component molecular ion group in the mass spectrum, and an aromatic:saturated C-H integral ratio of 6:18 in the pmr spectrum, (the chemical shifts of the dimethylamino and the two dimethylsulfamoyl group protons were distinguished). The positions of electrophilic substitution were determined on the basis of the appearance of the aromatic region. This contained an AA′BB′ pattern due to two pairs of equivalent protons, one of which was significantly shielded (δ 6.92), which indicated that the 4′-substituent was the dimethylamino group. In addition, there was an AB pattern with a coupling constant of 1.5 Hz. The benzo-ring was consequently disubstituted, and the two aromatic protons were *meta* to one another, (the *para*-coupling constant is virtually zero, and the *ortho*-coupling constant is about 8 Hz, on the basis of the pmr spectra of other derivatives described in this paper). The chemical shifts of H-5 and H-7 have been assigned on the basis of the predominance of the anisotropic effects of the sulfamoyl groups.

The formation of compound II can be explained as follows: under the reaction conditions the dimethylamino substituent would be protonated. The chlorohydrin should therefore form by reaction at the carbonyl group adjacent to the unsubstituted phenyl ring-protonation on the oxygen atom of the other carbonyl group would be less favoured due to electron-withdrawal by the substituent. The preference for further substitution in the benzo-ring can be attributed to the *meta*-directing influence of the 6-chlorosulfonyl substituent. The 3′-position is deactivated to electrophilic attack, and the 2′-position is sterically hindered.

The uv spectra of all of the dimethylsulfonamides Ia-VIIIa showed an absorption at 300-320 nm, in agreement with the reported data for benzofuran [12,13]. The uv spectrum of the *N,N*-dimethylamino derivative (II) contained an additional long wavelength band (406 nm), which is probably due to the auxochrome.

A larger excess of chlorosulfonic acid (10 molar equivalents), with 4,4′-dichlorobenzil, followed by reaction of the crude product with dimethylamine, afforded the 5,3′-bis(*N,N*-dimethylsulfonamide) IIIa. The structure was assigned on the basis of microanalytical, uv and ms data, together with the pmr spectrum of the diethylamide IIIb. The mass spectrum of IIIa contained a four-component molecular ion group (intensity ratio 27:27:9:1), which confirmed the presence of three chlorine atoms. The pmr spectrum of IIIb indicated that the two *N,N*-diethylsulfamoyl substituents contained methyl and methylene protons whose respective environments were not readily distinguished for the two groups. The aromatic region contained an ABC pattern for the 2-aryl ring, the position of substitution being assigned with regard to electronic and steric factors, as previously mentioned. The benzo-ring gave rise to two singlets, indicating that the protons concerned were H-4 and H-7 with the *para*-coupling constant being negligible. A number of other derivatives were prepared (IIIc-IIIg).

The reaction has been successful with 4,4′-dimethyl- and 3,3′-dibromobenzil, and in each case the bis(*N,N*-dimethylsulfonamides) IVa,V have been fully authenticated by microanalytical and spectral data. The pmr spectrum of IVa allowed the assignment of H-4 and H-7, as $^{4}J_{CH_3,\ H\text{-}7}$ caused broadening of the H-7 resonance signal compared with the width of the resonance signal due to H-4.

We have also shown that bis(*N,N*-dimethylsulfonamides) VI-VIII can be obtained from 2,2′- and 3,3′-dichlorobenzil, and 3,3′-dimethylbenzil, on the evidence of microanalytical and spectral data. However, in these instances the pmr spectra were complex, and the positions of electrophilic substitution could not be determined.

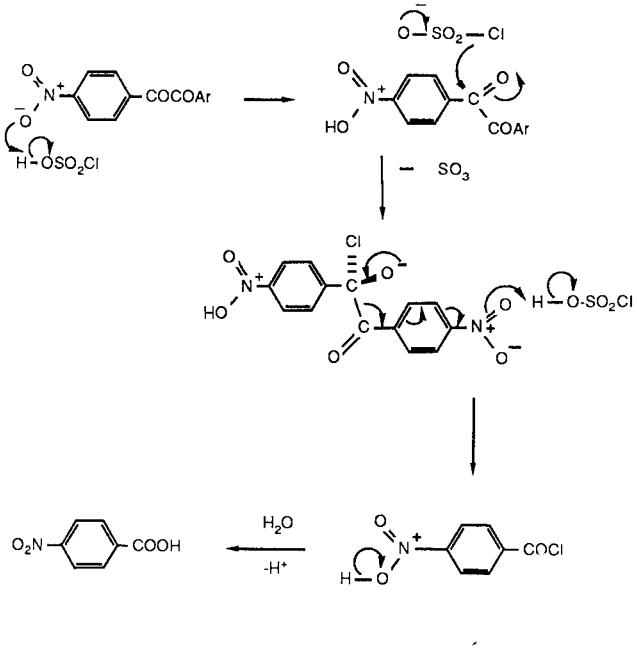
Attempts to chlorosulfonate 4,4′-dimethoxybenzil by treatment with chlorosulfonic acid (6 molar equivalents) at 0°, or in solution in chloroform, were unsuccessful. Extensive decomposition (charring) was observed; initial demethylation may well occur.

We have examined the reaction of 3,3′- and 4,4′-dinitrobenzil with a large excess of chlorosulfonic acid (12 molar equivalents) at 85°, in order to determine the influence of electron-withdrawing substituents. The only products which could be isolated were 3- and 4-nitrobenzoic acid

respectively. In these reactions the intermediate chlorohydrins may be destabilised due to the electron-withdrawing substituent, (Scheme 2).

Scheme 2

Decomposition of 4,4'-Dinitrobenzil



EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. The ir spectra were measured as nujol mulls with a Perkin Elmer 257 spectrophotometer, and the uv spectra in chloroform with a Unicam SP1800 spectrophotometer. The pmr spectra were determined with a Bruker WP80 spectrometer using tetramethylsilane as internal reference standard. The ABC analyses were approximated to first-order, and the AA'BB' analyses to AB. Mass spectra were recorded with a VG micromass V15 instrument. Tlc was carried out using Camlab Polygram silica gel plates sensitised to uv 254 nm.

Preparation of Substituted Benzils.

4,4'-Dichlorobenzil.

A concentrated solution of potassium cyanide (30 g, 0.05 mole) in water (20 ml) was added to a hot stirred solution of 4-chlorobenzaldehyde (100 g, 0.07 mole) in ethanol (500 ml). The mixture was heated under reflux for 2 hours, poured onto ice and then extracted with ether (3 x 100 ml). The combined extracts were washed with 10% sodium hydrogen carbonate solution (2 x 100 ml), sodium hydrogen sulfite solution (2 x 50 ml), saturated sodium chloride solution (2 x 100 ml), dried (magnesium sulfate), and the filtrate evaporated under reduced pressure to give an oil (200 g). The oil was heated with concentrated nitric acid (170 ml, 4 moles) on a steam bath for 6 hours. The solution was poured onto ice, the precipitate was filtered off and washed with water (6 x 100 ml). Recrystallisation from ethyl acetate gave 4,4'-dichlorobenzil as yellow needles (96 g, 48%), mp 199° (lit [14] 199°).

Application of the same procedure afforded the following substituted benzils: 3,3'-Dichloro- (45%), mp 114-116° (lit [15] 115°); 2,2'-Dichloro- (56%), mp 130-132° (lit [15] 132°); 4,4'-Dimethyl- (35%), mp 103-105° (lit [16] 104°); 3,3'-Dimethyl- (25%), mp 100-102° (lit [16] 102°); 3,3'-Dibromo- (25%), mp 122-123° (lit [17] 124°).

3,3-Dinitrobenzil

Benzil was nitrated by the use of a mixture of potassium nitrate and concentrated sulfuric acid as previously described [18] to give 3,3'-dinitrobenzil as yellow crystals from glacial acetic acid (86%), mp 132-133° (lit [18] 132°).

4,4-Dinitrobenzil.

A mixture of benzoin acetate [14] (200 g, 0.78 mole), ammonium acetate (60 g, 0.78 mole) and acetic acid (250 ml) was refluxed for 2 hours. The solution was poured onto ice and extracted with ether (3 x 100 ml). The combined extracts were washed with water (4 x 100 ml), saturated sodium chloride solution (3 x 50 ml) and dried (magnesium sulfate). Evaporation under reduced pressure gave crude 2-methyl-4,5-diphenyloxazole as a brown oil (250 g). The oxazole (100 g, 0.40 mole) was heated with a mixture of concentrated nitric acid (200 ml) and concentrated sulfuric acid (150 ml) at 50° for 15 minutes. Addition of ice and recrystallisation from glacial acetic acid gave 2-methyl-4,5-di(4'-nitrophenyl)-oxazole as yellow plates (130 g, 93%), mp 240-243° (lit [19] 242°). The di(4'-nitrophenyl)oxazole (100 g, 0.3 mole) was refluxed for 2 hours with bromine (190 g, 1.2 moles) in glacial acetic acid (250 ml) - water (10 ml). Addition of ice and recrystallisation from glacial acetic acid gave 4,4'-dinitrobenzil as yellow needles (82 g, 88%), mp 212-213° (lit [19] 214°).

4-(*N,N*-Dimethylamino)benzil.

A solution of 4-(*N,N*-dimethylamino)benzaldehyde (50 g, 0.33 mole), benzoin (32 g, 0.16 mole) in ethanol (200 ml) was refluxed for 2 hours with a solution of potassium cyanide (22 g, 0.33 mole) in water (20 ml). The solution was poured onto ice, and the precipitate recrystallised from ethanol to give 4-(*N,N*-dimethylamino)benzoin as yellow needles (30 g, 77%), mp 158-160° (lit [18] 159-160°). The product (30 g, 0.12 mole) was refluxed for 5 hours with a solution of copper sulfate (50 g) and pyridine (100 ml) in water (50 ml). The dark blue solution was cooled, the solid product collected and washed with water (5 x 100 ml). Recrystallisation from ethanol gave 4-(*N,N*-dimethylamino)benzil as yellow plates (18 g, 61%), mp 115-116° (lit [20] 116°).

3,6,4'-Trichloro-2-phenylbenzofuran-5-(*N,N*-dimethylsulfonamide) (Ia).

A mixture of 4,4'-dichlorobenzil (10 g, 0.04 mole) and chlorosulfonic acid (25 g, 0.20 mole) was heated at 80° for 1 hour. The solution was poured onto ice to give yellow crystals of the crude sulfonyl chloride (12 g, 83%), mp 138-140°.

A solution of the sulfonyl chloride (0.005 mole) in methanol (15 ml) was treated with a 40% aqueous solution of dimethylamine (0.015 mole). The mixture was left for 4 hours, added to ice-water (150 ml), and the precipitate recrystallised from methanol to give the *N,N*-dimethylsulfonamide Ia (40%), mp 150-153°; uv: 320 nm (47000); ir: 1600 (Ar C=C), 1340, 1160 cm^{-1} (SO_2); pmr (hexadeuteriodimethylsulfoxide-deuteriochloroform): δ 2.8 (s, 6H, Me_2N), 7.65 (d, 2H, H-2', H-6'), 8.05 (d, 2H, H-3', H-5'), 8.15 (s, 2H, H-4, H-7); ms: 409, 407, 405, 403 (M^+); tlc (ethyl acetate-cyclohexane, 2:5): one spot R_F 0.65.

Anal. Calcd. for $C_{16}H_{12}Cl_3NO_3S$: C, 47.5; H, 3.0; N, 3.5. Found: C, 47.7; H, 3.1; N, 3.2.

3,6,4'-Trichloro-2-phenylbenzofuran-5-sulphonyl Azide (Ib).

A solution of the sulfonyl chloride (0.005 mole) in acetone (40 ml) was stirred with sodium azide (0.01 mole) in water (10 ml) for 3 hours. Addition of ice-water (200 ml) gave, after recrystallisation from aqueous acetone, the sulfonyl azide Ib (85%), mp 154-155°.

Anal. Calcd. for $C_{14}H_6Cl_3N_3O_3S$: C, 41.7; H, 1.5; N, 10.4. Found: C, 42.0; H, 1.5; N, 10.6.

3,6,4'-Trichloro-2-phenylbenzofuran-5-sulfonyl Hydrazide (Ic).

The sulfonyl chloride (0.01 mole) was reacted with 98% hydrazine hydrate (0.02 mole) in methanol (25 ml) at room temperature for 3 hours. Addition of ice-water (100 ml) and recrystallisation from ethanol gave the hydrazide (Ic) (91%), mp 240-243°; ir: 3500, 3300 (NH_2), 1340, 1160 cm^{-1} (SO_2); tlc (ethyl acetate-cyclohexane, 2:3): one spot R_F 0.25.

Anal. Calcd. for $C_{14}H_9Cl_3N_2O_3S$: C, 42.9; H, 2.3; N, 7.15. Found: C,

42.6; H, 2.5; N, 6.9

3,6,4'-Trichloro-2-phenylbenzofuran-5-acetone Sulfonyl Hydrazone (Id).

The sulfonyl hydrazide Ic was warmed with acetone (20 ml) for 15 minutes. The solution on cooling gave the acetone sulfonyl hydrazone (Id) (73%), mp 186-187°; ir: 3200 (NH), 1600 (Ar C=C), 1345, 1175 cm^{-1} (SO_2).

Anal. Calcd. for $C_{17}H_{13}Cl_3N_2O_3S$: C, 47.3; H, 3.0; N, 6.5. Found: C, 47.0; H, 3.0; N, 6.6.

3,6,4'-Trichloro-2-phenylbenzofuran-5-benzaldehyde Sulfonyl Hydrazone (Ie).

The sulfonyl hydrazide Ic was warmed with freshly redistilled benzaldehyde (1 molar equivalent) in methanol for 15 minutes. The precipitate obtained on cooling, after recrystallisation from ethanol, gave the benzaldehyde sulfonyl hydrazone Ie (62%), mp 256-257°; ir: 3300 (NH), 1600 (Ar C=C), 1330, 1160 cm^{-1} (SO_2).

Anal. Calcd. for $C_{21}H_{15}Cl_3N_2O_3S$: C, 52.5; H, 2.7; N, 5.8. Found: C, 52.6; H, 3.0; N, 5.8.

3,6,4'-Trichloro-2-phenylbenzofuran-5-anisaldehyde Sulfonyl Hydrazone (If).

Prepared as described for Ie. Recrystallisation from ethanol gave the anisaldehyde sulfonyl hydrazone If (56%), mp 164-166°; ir: 3300 (NH), 1600 (Ar C=C), 1325, 1165 cm^{-1} (SO_2).

Anal. Calcd. for $C_{22}H_{15}Cl_3N_2O_4S$: C, 51.8; H, 2.9; N, 5.5. Found: C, 52.0; H, 3.1; N, 5.8.

3-Chloro-4'-(*N,N*-dimethylamino)-2-phenylbenzofuran-4,6-bis(*N,N*-dimethylsulfonamide) (II).

A mixture of 4-(*N,N*-dimethylamino)benzil (10.1 g, 0.04 mole) and chlorosulfonic acid (58 g, 0.50 mole) was heated for 2 hours at 80-85°. The cold solution was poured onto ice, the precipitate was filtered off, washed with ice-water (3 x 50 ml) and filtration gave the disulfonyl dichloride (14.2 g, 76%), mp 60-63%.

A solution of the disulfonyl dichloride (0.005 mole) in methanol (15 ml) was treated with a 40% aqueous solution of dimethylamine (0.03 mole). The mixture was left for 4 hours, added to ice-water (150 ml), and the precipitate recrystallised from aqueous methanol to give the bis(*N,N*-dimethylsulfonamide) II (28 g, 57%), mp 205-206°; uv: 320 nm (31000), 406 (27000); ir: 1600 (Ar C=C), 1340, 1130 cm^{-1} (SO_2); pmr (hexadeuteriodimethylsulfoxide): δ 2.7, 2.9, 3.1 (3s, 3 x 6H, $2Me_2NSO_2$, Me_2N), 6.92 (d, 2H, H-3', H-5'; $J_{2',3'}$ = 9 Hz); 7.94 (d, 1H, H-7, $J_{5,7}$ = 1.5 Hz), 8.04 (d, 2H, H-2', H-6', $J_{2',3'}$ = 9 Hz), 8.3 (d, 1H, H-5; $J_{5,7}$ = 1.5 Hz); ms: 489, 487 (M^+); tlc (ethyl acetate-light petroleum, 40-60°, 2:3): one spot R_F 0.60.

Anal. Calcd. for $C_{20}H_{24}ClN_5O_5S$: C, 49.4; H, 4.9; N, 8.7; S, 13.2. Found: C, 49.1; H, 5.0; N, 8.5; S, 13.2.

3,6,4'-Trichloro-2-phenylbenzofuran-5,3'-bis(*N,N*-dimethylsulfonamide) (IIIa).

A mixture of 4,4'-dichlorobenzil (5 g, 0.02 mole) and chlorosulfonic acid (25 g, 0.20 mole) was heated to 80-85° for 3 hours. The solution was poured onto ice to give the disulfonyl dichloride (6 g, 67%), mp 148-151°. The bis(*N,N*-dimethylsulfonamide) IIIa was prepared as described for II. Recrystallisation from aqueous methanol gave IIIa (78%), mp 188-189°; uv: 320 nm (27000); ir: 1600 (Ar C=C), 1360, 1145 cm^{-1} (SO_2); ms: 517, 515, 513, 511 (M^+).

Anal. Calcd. for $C_{18}H_{17}Cl_3N_2O_5S_2$: C, 42.2; H, 3.3; N, 5.5. Found: C, 42.2; H, 3.2; N, 5.1.

3,6,4'-Trichloro-2-phenylbenzofuran-5,3'-bis(*N,N*-diethylsulfonamide) (IIIb).

This compound was prepared as described for IIIa. Recrystallisation from ethanol gave IIIb (65%), mp 128-129°; ir: 1595 (Ar C=C), 1355, 1160 cm^{-1} (SO_2); pmr (hexadeuteriodimethylsulfoxide): δ 1.1 (t, 12H, 4Me), 3.4 (q, 8H, $4CH_2$), 7.94 (d, 1H, H-5', $J_{5',6'}$ = 8.5 Hz), 8.24 (s, 1H, H-7), 8.29 (s, 1H, H-4), 8.32 (dd, 1H, H-6', $J_{2',6'}$ = 2.0 Hz, $J_{5',6'}$ = 8.5 Hz), 8.64 (d, 1H, H-2', $J_{2',6'}$ = 2.0 Hz); tlc (ethyl acetate-cyclohexane, 2:3): one spot R_F 0.50.

Anal. Calcd. for $C_{22}H_{25}Cl_3N_2O_5S_2$: C, 46.5; H, 4.4; N, 4.9. Found: C, 46.2; H, 4.6; N, 4.7.

3,6,4'-Trichloro-2-phenylbenzofuran-5,3'-disulfonyl diazide (IIIc).

This compound was prepared as described for Ib. Recrystallisation from aqueous acetone gave IIIc (68%), mp 159-161°; ir: 1600 (Ar C=C), 1365, 1160 cm^{-1} (SO_2); tlc (ethyl acetate-cyclohexane, 2:3): one spot R_F 0.60.

Anal. Calcd. for $C_{14}H_5Cl_3N_6O_5S_2$: C, 33.1; H, 0.9; N, 16.6. Found: C, 33.2; H, 1.2; N, 16.4.

3,6,4'-Trichloro-2-phenylbenzofuran-5,3'-disulfonyl Dihydrazide (IIId).

This compound was prepared as described for Ic, but with hydrazine hydrate (0.04 mole). Recrystallisation from methanol gave IIId (59%), mp 265-266°; ir: 1600 (Ar C=C), 1335, 1140 cm^{-1} (SO_2). This compound was converted into the following disulfonyl dihydrazones.

3,6,4'-Trichloro-2-phenylbenzofuran-5,3'-bis(acetone Sulfonyl Hydrazone (IIIe).

This compound was prepared as described for Id. Recrystallisation from acetone gave IIIe (67%), mp 201-203°; ir: 3200 (NH), 1600 (Ar C=C), 1340, 1150 cm^{-1} (SO_2).

Anal. Calcd. for $C_{20}H_{19}Cl_3N_4O_5S_2$: C, 42.4; H, 3.4; N, 9.9. Found: C, 42.6; H, 3.6; N, 10.2.

3,6,4'-Trichloro-2-phenylbenzofuran-5,3'-bis(benzaldehyde Sulfonyl Hydrazone) (IIIf).

This compound was prepared as described for Ie, but with benzaldehyde (2 mole equivalents). Recrystallisation from ethanol gave IIIf (79%), mp 162-164°; ir: 3300 (NH), 1600 (Ar C=C), 1345, 1150 cm^{-1} (SO_2).

Anal. Calcd. for $C_{28}H_{19}Cl_3N_4O_5S_2$: C, 50.5; H, 2.9; N, 8.5. Found: C, 50.8; H, 3.3; N, 8.7.

3,6,4'-Trichloro-2-phenylbenzofuran-5,3'-bis(anisaldehyde Sulfonyl Hydrazone) (IIIg).

This compound was prepared as described for IIIf, but with anisaldehyde (2 molar equivalents). Recrystallisation from ethanol gave IIIg (24%), mp 160-161°; ir: 3300 (NH), 1600 (Ar C=C), 1340, 1150 cm^{-1} (SO_2).

Anal. Calcd. for $C_{30}H_{23}Cl_3N_4O_7S_2$: C, 49.9; H, 3.2; N, 7.8. Found: C, 50.0; H, 3.6; N, 7.6.

3-Chloro-6,4'-dimethyl-2-phenylbenzofuran-5,3'-bis(*N,N*-dimethylsulfonamide) (IVa).

A mixture of 4,4'-dimethylbenzil (5 g, 0.02 mole) and chlorosulfonic acid (14.7 g, 0.13 mole) was heated under reflux in dry chloroform (100 ml) for 4 hours. The mixture was poured onto crushed ice, the chloroform layer was separated, washed with water (3 x 100 ml), saturated sodium chloride (2 x 50 ml) and dried (magnesium sulfate). The solvent was evaporated under reduced pressure to give the disulfonyl dichloride (2 g, 20%), mp 150-155°.

The bis(*N,N*-dimethylsulfonamide) IVa was prepared as described for II. Recrystallisation from methanol gave IVa (20%), mp 174-175°; uv: 300 nm (24000); ir: 1600 (Ar C=C), 1320, 1160 cm^{-1} (SO_2); pmr (hexadeuteriodimethylsulfoxide): δ 2.65 (s, 3H, Me), 2.70 (s, 3H, Me), 2.77 (s, 6H, Me_2NSO_2), 2.82 (s, 6H, Me_2NSO_2), 7.68 (d, 1H, H-5', $J_{5',6'}$ = 8.0 Hz), 7.88 (s, 1H, H-7), 8.04 (s, 1H, H-4), 8.22 (dd, 1H, H-6', $J_{2',6'}$ = 1.6 Hz, $J_{5',6'}$ = 8.0 Hz), 8.44 (d, 1H, H-2', $J_{2',6'}$ = 1.6 Hz); ms: 473, 471 (M^+); tlc (ethyl acetate-cyclohexane, 2:3): one spot R_F 0.40.

Anal. Calcd. for $C_{20}H_{23}ClN_2O_5S_2$: C, 51.0; H, 4.9; N, 5.9. Found: C, 50.7; N, 4.9; N, 5.8.

3-Chloro-6,4'-dimethyl-2-phenylbenzofuran-5,3'-disulfonyl Dihydrazide (IVb).

This compound was prepared as described for IIId. Recrystallisation

from aqueous methanol gave IVb (73%), mp 270-273°; ir: 3400, 3200 (NH), 1590 (Ar C=C), 1335, 1140 cm^{-1} (SO_2). This compound was converted into the following disulfonyl dihydrazones.

3-Chloro-6,4'-dimethyl-2-phenylbenzofuran-5,3'-bis(acetone Sulfonyl Hydrazone (IVc).

This compound was prepared as described for Id. Recrystallisation from acetone gave IVc (77%), mp 236-238°; ir: 3300 (NH), 1600 (Ar C=C), 1340, 1150 cm^{-1} (SO_2).

Anal. Calcd. for $C_{22}H_{25}ClN_4O_5S_2$: C, 50.3; H, 4.7; N, 10.7. Found: C, 50.0; H, 4.6; N, 10.5.

5,3'-Dibromo-3-chloro-2-phenylbenzofuran-6,4'-bis(*N,N*-dimethylsulfonamide) (V).

This compound was prepared as described for II. Recrystallisation from aqueous methanol gave the bis(*N,N*-dimethylsulfonamide) V (57%), mp 205-206°; uv: 320 nm (24000); ir: 1600 (Ar C=C), 1360, 1140 cm^{-1} (SO_2); pmr (hexadeuteriodimethylsulfoxide-deuteriochloroform): δ 2.99 (s, 12H, $2Me_2NSO_2$), 7.98 (d, 1H, H-4, $J_{4,7}$ = 0.3 Hz), 8.13 (dd, 1H, H-5', $J_{2',5'}$ = 0.8 Hz, $J_{5',6'}$ = 8.0 Hz), 8.27 (dd, 1H, H-6'; $J_{2',6'}$ = 1.5 Hz, $J_{5',6'}$ = 8.0 Hz), 8.31 (d, 1H, H-7, $J_{4,7}$ = 0.3 Hz), 8.48 (dd, 1H, H-2', $J_{2',5'}$ = 0.8 Hz, $J_{2',6'}$ = 1.5 Hz); ms: 604, 602, 600, 598 (M^+).

Anal. Calcd. for $C_{18}H_{17}Br_2ClN_2O_5S_2$: C, 35.9; H, 2.8; N, 4.7. Found: C, 35.6; H, 2.7; N, 4.6.

Bis(*N,N*-dimethylsulfonamide) from 2,2'-Dichlorobenzil (VI).

This compound was prepared as described for II. Recrystallisation from aqueous methanol gave the bis(*N,N*-dimethylsulfonamide) VI (23%), mp 178-180°; uv: 320 nm (25000); ir: 1600 (Ar C=C), 1340, 1150 cm^{-1} (SO_2); ms: 517, 515, 513, 511 (M^+).

Anal. Calcd. for $C_{18}H_{17}Cl_3N_2O_5S_2$: C, 42.2; H, 3.3; N, 5.5. Found: C, 42.0; H, 3.2; N, 5.3.

Bis(*N,N*-dimethylsulfonamide) from 3,3'-Dichlorobenzil (VII).

This compound was prepared as described for II. Recrystallisation from aqueous methanol gave the bis(*N,N*-dimethylsulfonamide) VII (34%), mp 122-123°; uv: 320 nm (28000); ir: 1600 (Ar C=C), 1355, 1145 cm^{-1} (SO_2); ms: 517, 515, 513, 511 (M^+).

Anal. Calcd. for $C_{18}H_{17}Cl_3N_2O_5S_2$: C, 42.2; H, 3.3; N, 5.5. Found: C, 42.3; H, 3.6; N, 5.2.

Bis(*N,N*-dimethylsulfonamide) from 3,3'-Dimethylbenzil (VIII).

This compound was prepared as described for II. Recrystallisation from methanol gave the bis(*N,N*-dimethylsulfonamide) (VIII) (56%), mp 248-250°; ir: 1600 (Ar C=C), 1340, 1155 cm^{-1} (SO_2).

Anal. Calcd. for $C_{20}H_{23}ClN_2O_5S_2$: C, 51.0; H, 4.9; N, 5.9. Found: C, 50.8; H, 5.0; N, 6.0.

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