The combined extracts were concentrated by distilling the solvents at atmospheric pressure. When the volume had been reduced to 50 ml, dry benzene (10 ml) was added and the distillation continued until near dryness. The residue was treated with hexamethyldisilazane (5.0 g, 0.031 mol) and a trace of sand. The mixture was refluxed for several hours and then analyzed by glpc using a 15 ft × 0.125 in. column packed with 5% SE-30 on Chromosorb W at 110° (Table IX). Relative yields for hydrolysis of the isomeric esters and conversion into the silyl ethers were determined using authentic samples. Identification of the glpc peaks from the *m*-nitrophenylsulfonoxylation reaction was accomplished not only by comparison of retention times with authentic esters but also by trapping samples from the chromatographic column and comparing their infrared spectra to those of authentic samples.

Essentially the same procedure was used for the competitive reactions with other substrates with the minor differences given in Table IX.

Kinetics.—The procedure previously described[1b] was followed to titrate iodometrically for the disappearance of the peroxide content of the reaction mixtures.

Registry No.—Bromobenzene, 108-86-1; methyl benzoate, 93-58-3; nitrobenzene, 98-95-3; anisole, 100-66-3; *m*-nitrobenzenesulfonyl peroxide, 6209-71-8; benzene, 71-43-2; mesitylene, 108-67-8; *p*-nitrobenzenesulfonyl peroxide, 6209-72-9.

Acknowledgment.—We wish to thank Dr. Robert L. Waller for providing some of the kinetic data involving methyl benzoate.

The Reaction of Arylsulfonyl Azides with *N*-Methylindole

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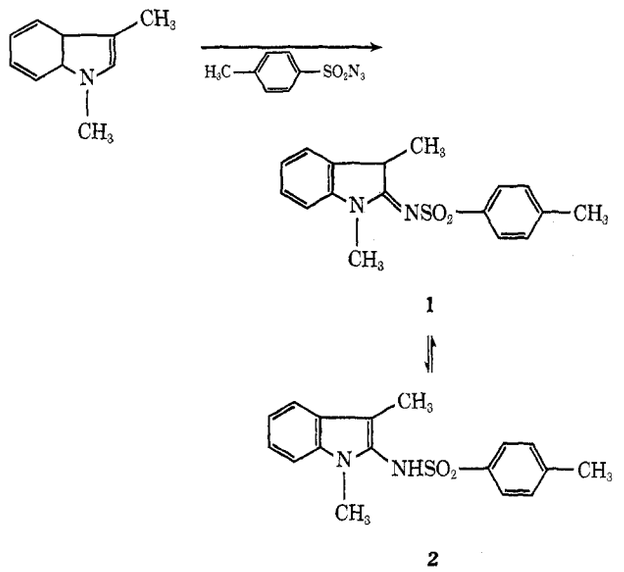
Received July 25, 1972

The reaction of several substituted arylsulfonyl azides with *N*-methylindole using *p*-dioxane as solvent yielded mixtures of the expected 2-sulfonamido and the unexpected 3-sulfonamido derivatives. In solution (DMSO-d_6) the 2-sulfonamides showed tautomeric equilibrium between the amino and the imino forms, whereas in crystalline form they existed mainly as the imino tautomers. The corresponding 3-sulfonamides existed only in the amino form. Using ethanol as solvent, the reaction of arylsulfonyl azides with *N*-methylindole afforded *N*-(3-diazo-1-methyl-2-indolinylidene)benzenesulfonamides. The same diazo compounds were obtained by treating the 2-sulfonamido derivatives with an excess of the appropriate arylsulfonyl azide, thereby providing the first example of a diazo transfer reaction to an amidine.

During the past several years Bailey and coworkers[1-5] have reported the results of their investigations on the reaction of arylsulfonyl azides with indole and alkylindoles. According to them the addition of *p*-toluenesulfonyl azide to 1,3-dimethylindole yielded an equilibrium mixture containing the 2-sulfonamido derivatives **1** and **2**. Bailey, *et al.*,[4] observed by nmr that the equilibrium between the tautomers **1** and **2** was solvent dependent, the imino form **1** predominating in chloroform while in dimethyl sulfoxide the amino form **2** predominates. In mixtures of these two solvents, both tautomers were present in appreciable amounts. We have investigated the above tautomeric equilibrium as a function of substituents on the arylsulfonyl azide. During the course of this study it was found that *N*-methylindole was more amenable to study the tautomeric equilibrium ratios than indole or dimethylindole used by Bailey, *et al.*[2,4]



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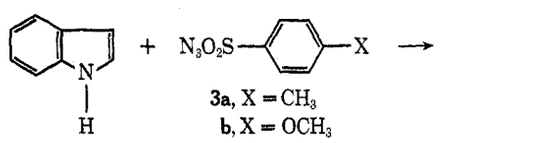
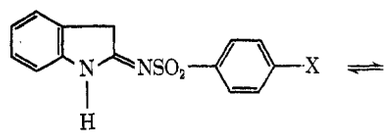
The Reactions of Arylsulfonyl Azides with Indole.—Our preliminary investigation based on the work reported by Bailey, *et al.*,[2] involved the reaction between three arylsulfonyl azides (**3a–c**) and indole. The

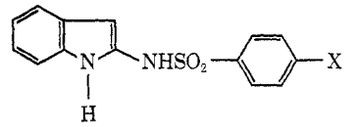


3a, X = CH_3
b, X = OCH_3
c, X = NO_2



(imino) A

4a, X = CH_3
b, X = OCH_3
c, X = NO_2

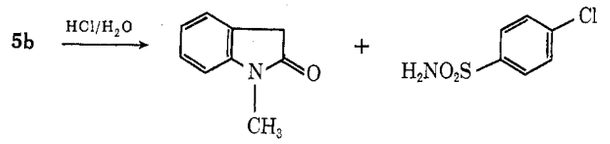


(amino) B

(1) A. S. Bailey and J. J. Merer, *J. Chem. Soc. C*, 1345 (1966).
(2) A. S. Bailey, N. C. Churn, and J. J. Wedgwood, *Tetrahedron Lett.*, 5953 (1968).
(3) A. S. Bailey, W. A. Warr, G. B. Allison, and C. K. Prout, *J. Chem. Soc. C*, 956 (1970).
(4) A. S. Bailey, R. Scattergood, and W. A. Warr, *Tetrahedron Lett.*, 2979 (1970).
(5) A. S. Bailey, A. J. Holton, and J. F. Seager, *J. Chem. Soc., Perkin Trans.* **1**, 1503 (1972).

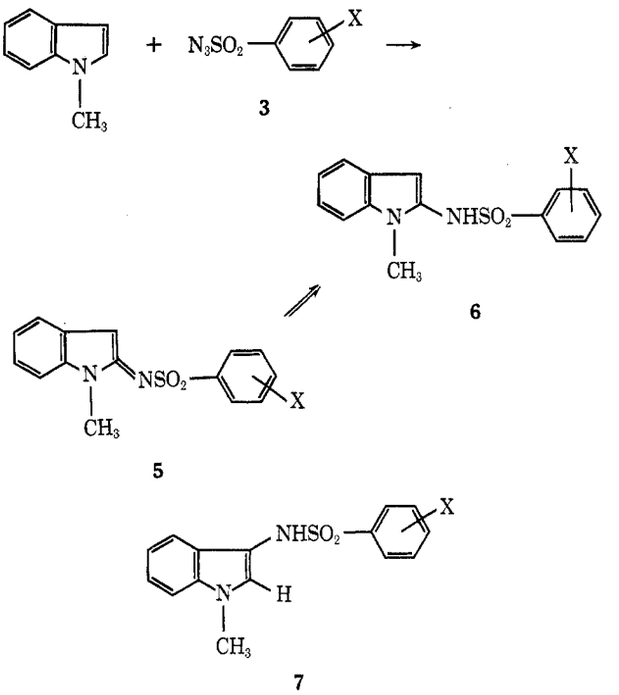
reactions were conducted by heating *p*-dioxane or ethanol solutions of indole and the appropriate sulfonyl azide at 75–80° during 6–48 hr. The resulting 2-indolinylidenebenzenesulfonamides (**4a–c**) gave satisfactory analyses and ir spectra. The tautomeric equilibrium between the amino and the imino forms was studied by nmr spectroscopy using DMSO-d_6 as solvent. The nmr spectra of the products **4a–c** could not be explained by assuming the presence of only the imino A and the amino B tautomers as reported by Bailey, *et al.*[2] This observation made it rather difficult for us to study the desired substituent effect on the amino–imino tautomerism. Therefore we decided to use *N*-methylindole instead.

The Reaction of Arylsulfonyl Azides with *N*-Methylindole.—The reaction of 13 substituted arylsulfonyl azides **3a–m** with *N*-methylindole was conducted by heating a solution of *N*-methylindole (0.01 mol) and the sulfonyl azide (0.015 mol) in *p*-dioxane at 75–80° during 18–24 hr. Cooling and diluting the reaction mixture with ethanol caused most of the 2-substituted product **5** to crystallize. After the separation of **5** by filtration, the filtrate was evaporated to dryness under reduced pressure and chromatographed over a column packed with silica gel. Elution with appropriate solvents afforded mostly **7** and small amount of **5**. In crystalline form, compounds **5** appear to exist mainly in the imino form, as shown by their ir spectra which had the characteristic C=N band at 1600 cm^{-1} and no absorption in the NH region. The location of the sulfonamido group at the 2 position of the indole ring was established by acid hydrolysis of **5b**, which yielded 1-methyloxindole (**8**) and *p*-chlorobenzenesulfonamide (**9**) in high yields.



8 **9**

Tautomerism of the 2-Sulfonamido Derivatives.—The 2-sulfonamido derivatives **5a–m** were found to exhibit amino–imino type of tautomerism on the basis of nmr spectroscopy using DMSO-d_6 and DMSO-d_6–$CDCl_3$ (15%) as solvents. Other nmr solvents, such as pure $CDCl_3$, could not be used owing to insufficient solubility of the products. The complete nmr data are given in Table I. The proton assignments are consistent with the proposed 2-substituted indole ring system. They are also in agreement with the assignments made by Bailey, *et al.*,[4] on similar compounds. In the nmr spectra the most significant differences were observed in the resonances due to the *N*-methyl protons as well as the proton(s) at the 3 position of the indole ring of structures **5a–m** and **6a–m**. For instance, in **5** the NCH_3 signal appeared around δ 3.4 and the two benzylic protons at the 3 position showed as a singlet near 4.2. On the other hand, the NCH_3 singlet of **6** appeared near δ 3.7 and the proton at the 3 position resonated as a singlet near 6.0. The relative ratios of the peaks around δ 4.2 (structure **5**) and 3.7 (structure **6**) were used to calculate the equilibrium ratios of these two tautomers in solution. The results are also included in Table I. It is clear from the results presented in Table I that in each case the imino



Compd	R group(s)
a	4-CH_3
b	4-OCH_3
c	4-$NHCOCH_3$
d	H
e	2,4,6-trimethyl
f	4-Cl
g	4-Br
h	3,4-di-Cl
i	3-NO_2-4-Cl
j	2,4,6-triisopropyl
k	4-NO_2
l	3-NO_2
m	2-NO_2

tautomer predominates in DMSO-d_6 solution. These results are opposite to those reported by Bailey, *et al.*,[4] in the case of 1,3-dimethylindole. They observed that in DMSO-d_6, the amino tautomer was the major species present. The addition of $CDCl_3$ (15%) shifted the tautomeric equilibrium between **5** and **6** even more in favor of the imino tautomer. This is consistent with the observations made by Bailey, *et al.*[4] This trend is the reverse of that reported for 2-aminoindoles.[6,7]

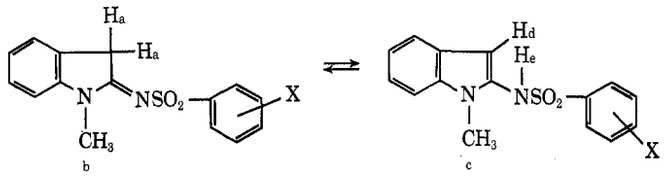
Further examination of Table I indicates that, in general, electron-withdrawing substituents on the benzenesulfonamido group reduce the percentage of amino tautomer in solution. Thus, the amino tautomer concentration ranges from a high of 20% with a *p*-methoxy group to a low of about 3% with an *o*-nitro group.

The Unexpected 3-Sulfonamido Derivatives (7a–m).—As mentioned earlier, the reaction of arylsulfonyl azides with *N*-methylindole yielded, in addition to the expected 2-sulfonamido derivatives **5**, the unexpected 3-sulfonamido derivatives **7**. In contrast to the results obtained with the 2-substituted products, compounds **7** were found by ir spectroscopy (which showed NH absorption but no C=N absorption) to exist as the amino tautomers in crystalline form. The nmr data {δ 6.8–7.0 (m, 1, C_2 of *N*-methylindole), 7.0–8.4 (m,

(6) J. Kebrle and K. Hoffmann, *Helv. Chim. Acta*, **39**, 116 (1956).
(7) W. J. Houlihan, Ed., "The Chemistry of Heterocyclic Compounds," Vol. 25, Wiley, New York, N. Y., 1972, p 50.

TABLE I

NMR DATA FOR 2-SULFONAMIDOINDOLINES AND RELATIVE EQUILIBRIUM RATIOS OF TAUTOMERS 5 AND 6[a]



5 6

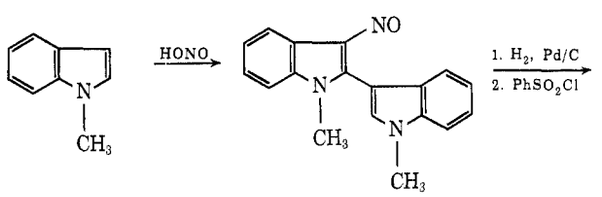
Substituent(s)		Nmr data, δ						Relative equilibrium ratios of tautomers 5 and 6			
								In DMSO-d_6		In DMSO-d_6–$CDCl_3$ (15%)	
No.	X	H_a	H_b	ArH	H_c	H_d	X	5	6	5	6
a	4-CH_3	4.24	3.36	7.17–8.35	3.64	6.00	3.93 (3, s, CH_3)	80	20	86	14
b	4-OCH_3	4.24	3.40	7.19–8.17	3.60	6.00	2.4 (3, s, OCH_3)	81	19	87	13
c	4-$NHCOCH_3$	4.17	3.44	6.70–8.15	3.57	5.89	10.30 (1, s, CH_3CONH), 2.10 (3, s, CH_3CONH)	81	19	87	13
d	H	4.20	3.33	6.94–8.21	3.67	5.90		84	16	88	12
e	2,4,6-Trimethyl	4.04	3.30	6.90–7.57	3.50	5.84	2.63 (6, s, *o*-CH_3), 2.23 (3, s, *p*-CH_3)	87	13	91	9
f	4-Cl	4.20	3.44	6.90–8.21	3.60	5.90		88	12	90	10
g	4-Br	4.17	3.30	6.94–8.00	3.54	5.84		89	11	90	10
h	3,4-di Cl	4.24	3.34	7.00–8.35	3.64	Not obsd		90	10	94	6
i	3-NO_2-4-Cl	4.27	3.40	7.06–8.60	3.67	Not obsd		90	10	93	7
j	2,4,6-Triisopropyl[b]	4.04	3.32	6.91–7.45	3.58	Not obsd	1.25 [18, m, $CH(CH_3)_2$], 2.93 [1, m, *p*-$CH(CH_3)_2$], 4.50 [2, m, *o*-$CH(CH_3)_2$]	91	9	94	6
k	4-NO_2	4.20	3.46	7.00–8.50	3.57	Not obsd		91	9	94	6
l	3-NO_2	4.24	3.47	7.00–8.73	3.60	Not obsd		92	8	93	7
m	2-NO_2	4.20	3.47	7.00–8.40	3.57	Not obsd		95	5	97	3

[a] The solvent used in all cases was DMSO-d_6 except as noted for j. Protons H_a, H_b, H_c, and H_d appeared as singlets and other protons as noted. Proton H_e was not observed in any spectra. Proton H_d was not observed when the amino tautomer concentration was less than about 10%. Equilibrium ratios for tautomers 5 and 6 are based on the relative absorptions due to protons H_a and H_c. The experimental error in these values is expected to be ±5%. [b] Solvent used was CD_3CN.

9, ArH), 9.4–10.1 (s, 1, $NHSO_2Ar$), 3.6–3.7 (s, 3, NCH_3), 1.0–2.3 (s, 3, CH_3), 2.4–2.38 (s, 3, OCH_3), 2.8–4.0 (m, 1, $CH(CH_3)_2$], etc.} using DMSO-d_6 as solvent ($CDCl_3$ was used as solvent for **7j**) supported the proposed structures. There was one exchangeable (D_2O) low-field signal integrating for one proton. There was no peak near δ 6.1 which would have been expected if the products were 2-sulfonamido derivatives. The presence of one proton NH signal indicated that these compounds did not exhibit amino–imino type of tautomerism and that they existed only in the amino form, both in crystalline form as well as in solution (DMSO-d_6). In order to substantiate the structures **7** assigned to these compounds we attempted the following alternate synthesis of **7d**.

Attempted Alternate Synthesis of 7d.—The nitrosation of 1-methylindole led to the formation of the undesirable 1-methyl-2-(1-methylindol-3-yl)-3-nitrosoindole (**10**). Similar results have been reported for the nitrosation of indoles unsubstituted at the 2 position.[8] The nitroso compound **10** could be readily reduced and treated with benzenesulfonyl chloride to yield the sulfonamido derivative **11**. Therefore the alternate synthesis of **7d** could not be accomplished using this approach.

Preparation of Model Compounds.—Since we were unsuccessful in achieving an independent synthesis of compounds **7**, we decided to prepare certain model compounds and compare their nmr spectra with those of **7**.



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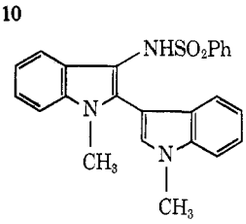
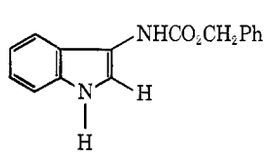
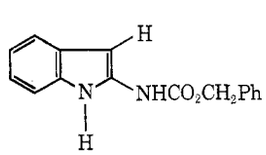


11

Carbobenzoxy-2- (**12**) and -3-aminoindoles (**13**) were chosen for this purpose. Compound **12** was prepared according to the procedure reported by Rinderknecht, *et al.*[9] Compound **13** was prepared analogously *via*



13

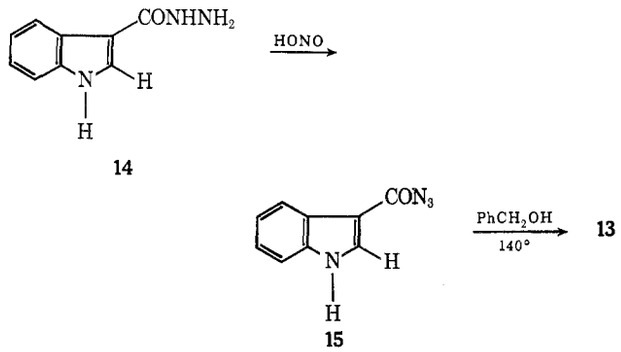


12

(8) W. J. Houlihan, Ed., "Indoles," Part II, Wiley, New York, N. Y., 1972, p 541.

(9) H. Rinderknecht, H. Koechlin, and C. Niemann, *J. Org. Chem.*, **18**, 971 (1953).

Curtius rearrangement of indole-3-carbonyl azide (**15**) in benzyl alcohol. The carbonyl azide **15** was prepared by treatment of the known indole-3-carboxylic acid hydrazide (**14**) with nitrous acid.[9]

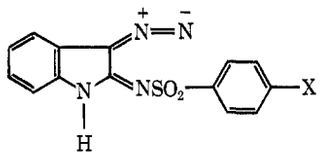


The nmr spectra of compounds **12** and **13** showed that in solution (DMSO-d_6) both of them exist in the amino tautomeric form as shown. Each compound had two low-field (δ 10–12) exchangeable (D_2O) peaks which integrated cleanly for one proton (NH) each. Hence compounds **12** and **13** were considered satisfactory models for the isomers **5** and **7**, respectively.

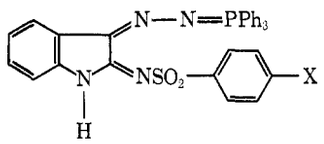
Further examination of the nmr spectrum of **12** showed that there was a doublet at δ 6.0 attributed to the C_3 proton of the indole ring. This assignment is consistent with the work of Witkop, *et al.*[10,11] This observation further supports the structures assigned to compounds **5**, since all of them had a peak (assigned to the amino tautomer) in this region of the nmr spectrum. The C_2 proton of the indole ring of **13** appeared in the aromatic region as was observed in the nmr spectra of compounds **7**. These results, which are also consistent with those reported by Witkop, *et al.*,[10,11] further substantiate the position of the sulfonamido group in compounds **7**.

A New Diazo Transfer Reaction.—The transfer of the diazo group from arylsulfonyl azides to an active methylene compound has been known for quite some time.[12] Nearly all of the reported examples have involved the transfer of a diazo group to the α carbon of carbonyl compounds.[12] In addition, the transfer of diazo group from sulfonyl azides generally requires the presence of a base catalyst.[12,13] The course of the reaction of arylsulfonyl azides with 1-methylindole using *p*-dioxane was different from that using ethanol as solvent.

The reaction of sulfonyl azides **3a** and **3f** with *N*-methylindole using ethanol as solvent gave the corresponding *N*-(3-diazo-1-methyl-2-indolinylidene)benzenesulfonamides **16a, b**. The reactions were followed by thin layer chromatography, which showed the formation of small amounts of the amidines **5a** and **5f** as intermediates which led to the diazo compounds **16a,b** as final products. This observation was further substantiated by the conversion of compound **5a** to **16a** in the presence of ethanol and the sulfonyl azide **3a**. The diazo compounds **16a,b** were light sensitive and difficult to isolate in pure form. However, treatment of these compounds with triphenylphosphine[14] afforded crystalline triphenylphosphine derivatives **17a,b** which were stable and gave satisfactory analyses. To the best of our knowledge this is the first example of a diazo transfer reaction to an amidine such as **5a** or **5f**. In addition compounds **16a,b** were formed without the aid of any added catalyst, unlike the normal diazo transfer reactions, which are base catalyzed. The isolation of **16** from the reaction of **5** with arylsulfonyl



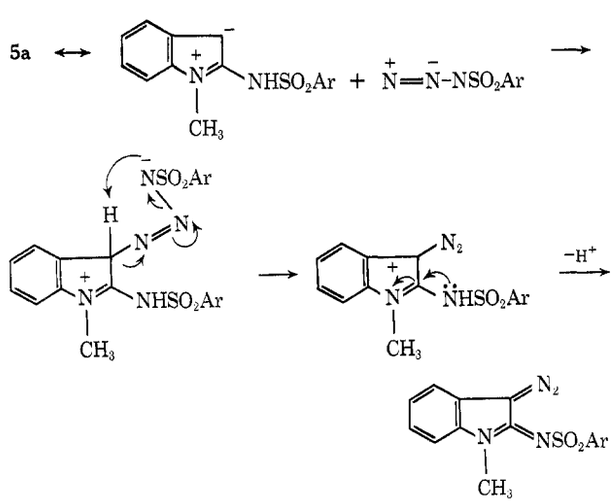
16a, X = CH_3
b, X = Cl



17a, X = CH_3
b, X = Cl

azides is of great interest regarding the mechanism of the reaction of azides with indoles.

Since the transfer of diazo group from sulfonyl azides is supposed to involve a carbanion as the reactive species, the following mechanism could be used to explain the formation of the diazo compounds **16**. According to Regitz,[12] the rate of the triethylamine-catalyzed diazo transfer reaction decreases with decreasing polarity of the solvent. Perhaps the same reasoning can be used to explain the reason why the diazo compounds **16** are formed in ethanol and not in *p*-dioxane, because ethanol is more polar than *p*-



dioxane. When an ethanol solution of the 2-sulfonamido derivative **5f** was heated with a differently substituted sulfonyl azide **3a** or **3d**, the same diazo compound **16b** was obtained. These experiments substantiate our proposed mechanism for the above diazo transfer reaction.

(10) L. A. Cohen, J. W. Daly, H. Kny, and B. Witkop, *J. Amer. Chem. Soc.*, **82**, 2184 (1960).

(11) R. A. Heacock, O. Hutzinger, B. D. Scott, J. W. Daly, and B. Witkop, *ibid.*, **85**, 1825 (1963).

(12) M. Regitz, "Newer Methods of Preparative Organic Chemistry," Vol. VI, Academic Press, New York, N. Y., 1971, p 81; M. Regitz, *Synthesis*, 351 (1972).

(13) R. A. Abramovitch and T. Takaya, *J. Org. Chem.*, **37**, 2022 (1972).

(14) M. Regitz and G. Himbert, *Tetrahedron Lett.*, 2823 (1970).

Experimental Section

Melting points were determined on a Thomas-Hoover Unimelt apparatus and are corrected. A Beckman IR-8 spectrophotometer was used to determine the ir spectra. The nmr spectra were run using a Varian A-60 spectrometer using tetramethylsilane as internal standard. The elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. Column chromatography was done using a 3 × 60 cm² glass column packed with silica gel. For thin layer chromatography (tlc), glass microscope slides coated with silica gel G were used. The spots on these slides were detected by iodine. *N*-methylindole was prepared from indole and methyl iodide using the procedure of Alder and Stein.[15] Methyl indole-3-carboxylate was prepared from the commercially available indole-3-carboxylic acid using the procedure of Millich and Becker.[16] It was converted to indole-3-carboxylic acid hydrazide by the procedure reported by Brown, *et al.*[17] The substituted arylsulfonyl azides **3** were prepared by treating the appropriately substituted benzenesulfonyl chlorides with sodium azide according to the method of Leffler and Tsuno.[18] All except one (**3j**) of the arylsulfonyl azides used in this study have previously been reported in the literature. Analytical data on compound **3j** prepared according to the general procedure are given below.

2,4,6-Triisopropylbenzenesulfonyl Azide (3j).—The title compound was prepared in 80% yield: mp 41–43°; ir (Nujol) 2120 (N_3) and 1164 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.25 (s, 2, ArH), 4.10 [m, 2, J = 6 Hz, ortho C**H**[CH_3)$_2$], 2.97 [m, 1, J = 7 Hz, para C**H**(CH_3)$_2$], 1.30 [d, 12, J = 6 Hz, ortho CH(C**H**$_3$)$_2$], and 1.25 [d, 6, J = 7 Hz, para CH(C**H**$_3$)$_2$]. *Anal.* Calcd for $C_{15}H_{23}N_3O_2S$: C, 58.23; H, 7.49; N, 13.58. Found: C, 58.21; H, 7.69; N, 13.42.

Preparation of *p*-Methyl-*N*-(2-indolinylidene)benzenesulfonamide (4a).—Indole (0.9 g, 0.0077 mol) and *p*-toluenesulfonyl azide (2 g, 0.01 mol) were heated at 75–80° for 48 hr in *p*-dioxane (5 ml). The solution was then diluted with 3 ml of ether and 3 ml of methanol, precipitating 1.0 g (46%) of **4a**: mp 234–236°; ir (Nujol) 3150 (NH), 1580, 1610 (C=N), and 1140 cm^{-1} (SO_2); nmr (DMSO-d_6) δ 11.50 (s, NH), 10.08 (s, NH), 8.00–6.65 (m, 8, ArH), 5.80 (s), 4.10 (s), 3.57 (s, shoulder), and 2.37 (s, 3, CH_3). *Anal.* Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.91; H, 4.92; N, 9.78; S, 11.19. Found: C, 62.85; H, 4.99; N, 9.81; S, 11.05.

Preparation of *p*-Methoxy-*N*-(2-indolinylidene)benzenesulfonamide (4b).—Indole (1 g, 0.0085 mol) and *p*-methoxybenzenesulfonyl azide (2 g, 0.0094 mol) were heated at 80° for 26 hr in *p*-dioxane (5 ml). The solution was diluted with 5 ml of methanol, precipitating 0.6 g (22%) of **4b**: mp 224–225° dec; ir (Nujol) 1580 (C=N), 1145, and 1135 cm^{-1} (SO_2); nmr (DMSO-d_6) δ 11.40 (s, NH), 10.70 (s, NH), 10.30 (s, NH), 8.00–6.80 (m, 8, ArH), 5.73 (s), 4.04 (s), 3.80 (s, OCH_3), 3.77 (s, OCH_3), and 3.53 (s). *Anal.* Calcd for $C_{15}H_{14}N_2O_3S$: C, 59.58; H, 4.66; N, 9.26; S, 10.60. Found: C, 59.33; H, 4.94; N, 9.55; S, 10.62.

Preparation of *p*-Nitro-*N*-(2-indolinylidene)benzenesulfonamide (4c).—Indole (2 g, 0.017 mol) and *p*-nitrobenzenesulfonyl azide (4 g, 0.017 mol) were refluxed in 75 ml of ethanol for 6 hr. On cooling, the solution deposited 3.3 g (61%) of the product **4c**: mp 249–260° dec; ir (Nujol) 1560 (C=N), 1150, and 1145 cm^{-1} (SO_2); nmr (DMSO-d_6) δ 12.20 (s, NH), 11.40 (s, NH), 8.87 (m, 4, sulfonamide ArH), 7.91–7.00 (m, 4, indole ArH), 6.07 (d, J = 2 Hz), and 4.37 (s). *Anal.* Calcd for $C_{14}H_{11}N_3O_4S$: C, 52.99; H, 3.49; N, 13.24; S, 10.10. Found: C, 52.80; H, 3.62; N, 13.53; S, 10.16.

General Procedure for the Reaction of Substituted Arylsulfonyl Azides with *N*-Methylindole and Isolation of Products 5a–m and 7a–m.—*N*-Methylindole (1.3 g, 0.01 mol) was dissolved in 5 ml of dry *p*-dioxane. A 1.5 molar excess of the appropriately substituted arylsulfonyl azide (**3a–m**) was dissolved in this solution. The solution was heated (oil bath) and stirred at 75–80° for 18–24 hr. The solution was then cooled and diluted with about 25 ml of ethanol (heptane was used for **5j** and **7j**), causing the majority of 2-substituted product (**5a–7m**) to crystallize from the solution in each case. The filtrate was evaporated to dryness and chromatographed on a column packed with silica gel using chloroform (2:8:10 ether–hexane–chloroform used for **5j** and **7j**; 9:1 ethyl acetate–heptane for **5c** and **7c**; 9:1 benzene–ethyl acetate for **5b** and **7b**; 20:1 chloroform–ethyl acetate for **5i** and **7i**; methylene chloride for **5m**) for elution of the products. The fractions containing the 2-sulfonamido products (**5a–m**) were combined and evaporated to dryness. The residue thus obtained was recrystallized from ethanol and combined with the product obtained from dilution of the reaction mixutre. The combined total yield is reported in Table II. The fractions containing the 3-sulfonamido derivatives (**7a–m**) were similarly treated and the yields of these products are also reported in Table II. All other chromatographic fractions and all mother liquors from recrystallizations which showed a tlc-detectable amount of either isomer were combined and evaporated to dryness. The weight of this residue was less than 0.2 g in all cases. All compounds gave satisfactory elemental analyses. Meltlng points are also reported in Table II.

TABLE II[a]

ANALYTICAL DATA FOR 2-SULFONAMIDOINDOLINES **5a–m** AND 3-SULFONAMIDOINDOLINES **7a–m**

Compd	Mp, °C	Yield, %	Compd	Mp, °C	Yield, %
5a	189–191	47	**7a**	160–162	24
5b	197–199	44	**7b**	180–182	22
5c	260–262	67	**7c**	226–228	5
5d	143–144	54	**7d**	174–175	22
5e	209–210	34	**7e**	212–214	15
5f	189–191	60	**7f**	181–183	16
5g	202–203	49	**7g**	203–204	12
5h	208–209	63	**7h**	180–181	14
5i	212–214	82	**7i**	160–161	8
5j	172–174	32	**7j**	157–158	24
5k	243–244	72	**7k**	199–200	21
5l	194–195	74	**7l**	173–175	6
5m	208–210	75	**7m**	193–195	14

[a] Satisfactory analytical data (±0.4% for C, H, N, and S) were reported for all compounds listed in Table II.

Hydrolysis of *p*-Chloro-(*N*-methyl-2-indolinylidene)benzenesulfonamide (5f).—The title compound (1 g, 0.0031 mol) was refluxed for 10 hr in a solution containing 100 ml of ethanol and 3 ml of concentrated HCl. The mixture was evaporated to dryness under reduced pressure and the residue was chromatographed on silica gel, eluting the products with ether. The first fraction contained 0.55 g (92%) of *p*-chlorobenzenesulfonamide. It was recrystallized from ethanol–heptane, giving 0.5 g (84%) of pure *p*-chlorobenzenesulfonamide, mp 144–145° (lit.[19] mp 143–144°). The second fraction consisted of 1-methyloxindole in 87% crude yield. Recrystallization from heptane gave 0.3 g (66%) of pure 1-methyloxindole, mp 84–87° (lit.[6] mp 84–86°).

Attempted Preparation of *N*-(1-Methyl-2-indolinylidene)benzenesulfonamide(5d) *via* Sulfonation of 2-Amino-1-methylindole Hydroiodide.—In dry pyridine, 2-amino-1-methylindole hydroiodide (0.1 g) was dissolved and cooled to 0°. Benzenesulfonyl chloride (1 ml) was slowly added to it, causing the solution to turn black. The tlc of this solution showed a spot with low (0.1) R_f value (developed with chloroform) and one with a higher (0.7) R_f value. Neither spot corresponded to **5d** or **7d**. The use of other solvents such as ethanol, benzene, or THF in conjunction with triethylamine gave similar results.

Attempted Hydrolysis of *p*-Chloro-*N*-(1-methylindol-3-yl)benzenesulfonamide (7f).—A solution of the title compound (0.0 g, 0.00031 mol) in 15 ml of ethanol containing 1 ml of concentrated HCl was refluxed for 4 days. Upon work-up, 0.085 g (85%) of **7f** was recovered unchanged.

Preparation of 1-Methyl-2-(1-methylindol-3-yl)-3-nitrosoindole (10).—*N*-Methylindole (14.5 g, 0.123 mol) was dissolved in 500 ml of glacial acetic acid and stirred vigorously while sodium nitrite (10 g, 0.162 mol) in 14 ml of water was added to it dropwise. The temperature was maintained at below 15° throughout the addition. The solution was then diluted with 500 ml of ether and 500 ml of hexane. The mixture was cooled at 5° and, after 1 hr, the mother liquor was decanted from a black precipitated oil. The oil was triturated with ether and the brown-yellow solid was

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collected. The solid was washed with acetone to give a green solid, mp 220°, which upon crystallization from acetonitrile yielded green crystals, 3 g (20%) of compound **10**: mp 243–244°; ir (Nujol) 1560 cm^{-1} (N=O); nmr (DMSO-d_6) δ 7.10–8.30 (m, 9, ArH), 4.00 (s, 3, NCH_3), and 3.94 (s, 3, NCH_3). *Anal.* Calcd for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.22; N, 14.53. Found: C, 74.59; H, 5.72; N, 14.86.

Preparation of *N*-[1-Methyl-2-(1-methylindol-3-yl)indol-3-yl]-benzenesulfonamide (11).—A solution of compound **10** (1 g, 0.00345 mol) in 50 ml of ethanol was hydrogenated at 50 psi for 10 hr in the presence of 0.2 g of Adam's catalyst. The solvent was removed under reduced pressure and the oil was dissolved in 20 ml of dry pyridine. Benzenesulfonyl chloride (2 ml) was added to it and the solution was allowed to stand for 1 hr at room temperature. It was then poured into water and extracted with chloroform. The chloroform layer was separated and dried (Na_2SO_4) and the solvent was removed under reduced pressure, leaving a yellow-green oil. The oil was crystallized from ethyl acetate–heptane, yielding 0.85 g (60%) of **11**: mp 176–177°; ir (Nujol) 3270 (NH) and 1158 cm^{-1} (SO_2); nmr (DMSO-d_6) δ 9.64 (s, 1, NH), 3.77 (s, 3, NCH_3), and 3.50 (s, 3, NCH_3). *Anal.* Calcd for $C_{24}H_{21}N_3O_2S$: C, 69.37; H, 5.09; N, 10.11; S, 7.71. Found: C, 69.17; H, 5.17; N, 10.17; S, 8.04.

Preparation of Indole-3-carbonyl Azide (15).—To a solution of indole-3-carboxylic acid hydrazide (1 g, 0.0057 mol) in 10 ml of glacial acetic acid was added a solution of sodium nitrite (1.2 g, 0.0175 mol) in 5 ml of water in small portions. After the addition of 50 ml of HCl (5%), the mixture was poured into 500 ml of water and stirred for 20 min. Filtration yielded 1.05 g (100%) of **15**: mp 144° dec; ir (Nujol) 3250 (NH), 2145 (N_3), 2120 (N_3), and 1650 cm^{-1} (C=O); nmr (DMSO-d_6) δ 12.12 (s, 1, NH) and 7.00–8.33 (m, 5, ArH). *Anal.* Calcd for $C_9H_6N_4O$: C, 58.06; H, 3.25; N, 30.03. Found: C, 57.50; H, 3.26; N, 29.79.

Preparation of Carbobenzoxy-3-aminoindole (13).—Indole-3-carbonyl azide (1 g, 0.0054 mol) was added portionwise to a refluxing solution containing 30 ml of toluene and 2 ml of benzyl alcohol. The solvent was removed by evaporation at reduced pressure and the residue was recrystallized from benzene–heptane to yield 1.1 g (79%) of **13**, mp 148–155°. Repeated recrystallization from benzene–heptane yielded colorless crystals: mp 164–165°; nmr (DMSO-d_6) δ 10.69 (s, 1, NH), 9.41 (s, 1, NH), 7.88–6.79 (m, 10, aromatic and 2-indole H), and 5.18 (s, 2, OCH_2Ph). *Anal.* Calcd for $C_{16}H_{14}N_2O_2$: C, 72.17; H, 5.29; N, 10.52. Found: C, 72.37; H, 5.57; N, 10.76.

Preparation of Carbobenzoxy-2-aminoindole (12).—Indole-2-carbonyl azide (3 g, 0.016 mol) (prepared according to the procedure of Rinderknecht[9]) was added portionwise to a refluxing solution containing 40 ml of toluene and 6 g of benzyl alcohol. The reaction mixture was refluxed for an additional period of 2 hr and the toluene was removed by evaporation at reduced pressure. The resulting black residue was chromatographed over silica gel. Elution with methylene chloride yielded 45% of crude **12**, which was crystallized from benzene–heptane to give white crystals: mp 138–139° (lit.[9] mp 139–140°); nmr (DMSO-d_6) δ 10.65 (s, 1, NH), 10.29 (s, 1, NH), 7.57–6.80 (m, 9, ArH), 6.00 (d, 2, J = 4 Hz, C-3 indole H), and 5.20 (s, 2, OCH_2Ph).

Addition of *p*-Toluenesulfonyl Azide to *N*-Methylindole in Ethanol. Preparation of *p*-Methyl-*N*-(3-diazo-1-methyl-2-indolinylidene)benzenesulfonamide (16a).—A solution of *N*-methylindole (1.3 g, 0.01 mol) in 100 ml of ethanol was refluxed with **3a** (2.5 g, 0.0127 mol) for 20 hr. The solution deposited 1.0 g (33%) of **5a** which was collected. The filtrate was refluxed for an additional 20 hr after more of **3a** (1.0 g, 0.0051 mol) had been added. Upon cooling, the solution deposited 1.0 g of **16a**, mp 161–163°. The same product could be obtained in 61% yield by treating **5a** with a threefold excess of **3a** in refluxing ethanol for 1–2 days. This product was not obtained under the same conditions using *p*-dioxane as a solvent instead of ethanol. Compound **16a** was recrystallized from butanone: mp 165–166°; ir (Nujol) 2100 cm^{-1} (N_2). *Anal.* Calcd for $C_{16}H_{14}N_4SO_2$: C, 58.88; H, 4.32; N, 17.17. Found: C, 59.42; H, 4.47; N, 16.26.

Preparation of *p*-Methyl-*N*-[1-methyl-3-[(triphenylphosphoranylidene)hydrazono]-2-indolinylidene]benzenesulfonamide (17a).—Compound **16a** (0.1 g, 0.000306 mol) was refluxed with a solution of triphenylphosphine (0.1 g, 0.00035 mol) in 25 ml of ethanol for 2 hr. The solution deposited 0.11 g of **17a** and the concentration of the filtrate gave an additional 0.01 g of **17a** (total yield 67%): mp 206–207°; ir (Nujol) 1575 and 1510 cm^{-1}. *Anal.* Calcd for $C_{34}H_{29}N_4O_2PS$: C, 69.37; H, 4.97; N, 9.52; P, 5.26. Found: C, 69.19; H, 4.85; N, 9.45; P, 5.50.

Preparation of *p*-Chloro-*N*-[1-methyl-3-[(triphenylphosphoranylidene)hydrazono]-2-indolinylidene]benzenesulfonamide (17b).—*p*-Chloro-*N*-(1-methyl-2-indolinylidene)benzenesulfonamide (**5f**, 1.5 g, 0.0046 mol) was refluxed with a solution of *p*-chlorobenzenesulfonyl azide (2 g, 0.0092 mol) in 125 ml of ethanol for 66 hr. After cooling, 1.1 g (68%) of the intermediate *p*-chloro-*N*-(3-diazo-1-methyl-2-indolinylidene)benzenesulfonamide (**16b**) was collected. This material was recrystallized from ethanol and 0.3 g (0.00029 mol) of the purified material was refluxed with a solution of triphenylphosphine (0.3 g, 0.00095 mol) in ethanol for 3 hr. The solution deposited (in two crops) a total of 0.48 g (84%) of **17b**: mp 223–224° dec; ir (Nujol) 1510 and 1580 cm^{-1}. *Anal.* Calcd for $C_{33}H_{26}ClN_4O_2PS$: C, 65.07; H, 4.30; N, 9.20; Cl, 5.82; P, 5.09. Found: C, 65.01; H, 4.33; N, 9.45; Cl, 5.81; P, 5.10.

Registry No.—**3j**, 36982-84-0; **4aA**, 36982-85-1; **4aB**, 36982-86-2; **4bA**, 36982-87-3; **4bB**, 36982-88-4; **4cA**, 36982-89-5; **4cB**, 36982-90-8; **5a**, 36982-91-9; **5b**, 36982-92-0; **5c**, 36982-93-1; **5d**, 36982-94-2; **5e**, 36982-95-3; **5f**, 36982-96-4; **5g**, 36982-97-5; **5h**, 36982-98-6; **5i**, 36982-99-7; **5j**, 36983-00-3; **5k**, 36983-01-4; **5e**, 36983-01-4; **5m**, 36983-03-6; **6a**, 36983-04-7; **6b**, 36983-05-8; **6c**, 36983-06-9; **6d**, 36983-07-0; **6e**, 36983-08-1; **6f**, 36982-13-5; **6g**, 36982-14-6; **6h**, 36982-15-7; **6i**, 36982-16-8; **6j**, 36982-17-9; **6k**, 36982-18-0; **6l**, 36982-19-1; **6m**, 36982-20-4; **7a**, 36982-21-5; **7b**, 36982-22-6; **7c**, 36994-49-7; **7d**, 36982-23-7; **7e**, 36982-24-8; **7f**, 36982-25-9; **7g**, 36982-26-0; **7h**, 36982-27-1; **7i**, 36982-28-2; **7j**, 36982-29-3; **7k**, 36982-30-6; **7l**, 36982-31-7; **7m**, 36982-32-8; **10**, 36982-33-9; **11**, 36982-34-0; **12**, 20948-96-3; **13**, 36982-36-2; **15**, 36982-37-3; **16a**, 36994-50-0; **17a**, 36982-38-4; **17b**, 36982-39-5; *N*-methylindole, 603-76-9.

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