mp 341–344°[24]), collected by filtration, was washed again with water. The combined filtrate and washings were decolorized with charcoal, if necessary, and evaporated to dryness *in vacuo*. 4-Amino-2-butene-1-thiosulfuric acid (1.49 g, 90%) was recrystallized from H_2O–EtOH and obtained as shiny white flakes, mp 168–169° dec.

Anal. Calcd for $C_4H_9NO_3S$: C, 26.22; H, 4.95; N, 7.64; S, 34.99. Found: C, 26.32; H, 5.03; N, 7.69; S, 34.78.

4-Amino-2-butyne-1-thiosulfuric Acid (XVII).—To 43.5 g (0.112 mol) of sodium 4-phthalimido-2-butynylthiosulfate was added a solution of 7.19 g (0.144 mol) of 100% hydrazine hydrate (64% hydrazine in water) in 350 ml of MeOH. The yellow solution was stirred and gently refluxed for 1.5 hr. (A solid began to precipitate after *ca.* 15 min of heating.) A solution of 70 ml of glacial HOAc in 350 ml of MeOH was then added to the stirred reaction mixture which was then heated for an additional 20 min. The orange mixture was cooled and filtered. The filtrate was evaporated under reduced pressure at 40°, and the combined solid residues were extracted with three 250-ml portions of water. The insoluble phthalhydrazide (16.8 g, 93%) was collected by filtration and washed with 75 ml of water. The combined filtrate and washings were decolorized with charcoal and evaporated to dryness under reduced pressure at 50°. 4-Amino-2-butyne-1-thiosulfuric acid (11.7 g, 58%), after washing with EtOH, was recrystallized from water, giving the product as shiny off-white flakes, mp >170° dec.

Anal. Calcd for $C_4H_7NO_3S_2$: C, 26.51; H, 3.89; N, 7.73; S, 35.38. Found: C, 26.51; H, 3.94; N, 7.66; S, 35.22.

(24) H. D. K. Drew and H. H. Hatt, *J. Chem. Soc.*, 16 (1937).

Disproportionation of Bis(decylaminoethyl) Disulfide Thiosulfuric Acid Salt (X).—A solution of 2.73 g (0.005 mol) of X in 80 ml of MeOH was heated under reflux for 24 hr during which time H_2S was evolved. The solution was evaporated to dryness under reduced pressure and the residue was triturated with *ca.* 30 ml of hexane and cooled. The insoluble Bunte salt XI, 1.44 g (96%), was collected by filtration. The hexane filtrate was taken to dryness to give 1.07 g (92%) of the trisulfide XII, a tan-colored oil.

Anal. Calcd for $C_{24}H_{52}N_2S_3$: C, 62.00; H, 11.27; N, 6.03; S, 20.69. Found: C, 61.02; H, 11.09; N, 6.58; S, 21.75.

Registry No.—II, 31645-59-7; III, 31645-60-0; IV, 31645-61-1; V, 31645-62-2; VII, 31645-63-3; XII, 31645-64-4; XIII, 2697-60-1; XIV, 31645-66-6; XVI, 31645-67-7; XVII, 31645-68-8; *N*-(4-chloro-2-butenyl)phthalimide, 31645-84-8; *N*-(4-chloro-2-butynyl)phthalimide, 4819-69-6; sodium 4-phthalimido-2-butenylthiosulfate, 31645-86-0; sodium 4-phthalimido-2-butynylthiosulfate, 31645-87-1; hydrogen sulfide, 7783-06-4.

Acknowledgment.—We thank Dr. Thomas E. Fink, Arless E. Murray, Jr., and David Bower for their technical assistance and Dr. Thomas R. Sweeney for his interest in this investigation.

Carbodiimide–Sulfoxide Reactions. XII.[1] Reactions of Sulfonamides

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The reactions of aryl- and alkylsulfonamides with DMSO and DCC in the presence of anhydrous orthophosphoric acid has been shown to give *S,S*-dimethyl-*N*-sulfonylsulfilimines in high yields. *N*-Alkylsulfonamides cannot form sulfilimines but rather react slowly with DMSO and DCC to form *N*-alkyl-*N*-(1,3-dicyclohexyl-1-ureidomethyl)sulfonamides. A similar reaction of *N*-benzyl-*p*-toluenesulfonamide with DMSO and phosphorus pentoxide gave *N,N'*-methylenebis(*N*-benzyl-*p*-toluenesulfonamide) as the major product. *N*-Arylsulfonamides such as *p*-toluenesulfonanilide react with DMSO and DCC so as to introduce methylthiomethyl groups in either or both of the unsubstituted ortho positions. Several sulfonanilides containing methyl, nitro, and cyano substituents in the ortho positions of the aniline ring gave products in which methylthiomethyl groups were introduced on nitrogen or at an available ortho position. The very acidic sulfonamide saccharin did not react in a similar way but rather gave a 1:1 adduct with DCC in high yield.

In the preceding paper in this series[1] the previously described mild acid-catalyzed reactions of alcohols,[3] phenols,[4] enols,[5] and oximes[6] with dimethyl sulfoxide (DMSO) and dicyclohexylcarbodiimide (DCC) were extended to carboxylic acids, hydroxamic acids, and carboxylic acid amides. Simple primary amides of carboxylic acids were found to be readily converted into *N*-acyl-*S,S*-dimethylsulfilimines, while compounds such as benzanilide were completely inert and imides of various sorts reacted slowly to give either *N*-(methylthiomethyl) or *N*-(1,3-dicyclohexyl-1-ureidomethyl) derivatives. In the present paper we extend these studies to the reactions of several types of sulfonamides.

p-Toluenesulfonamide (**1**) reacted quite readily with DMSO and DCC in the presence of 0.5 equiv of anhydrous orthophosphoric acid to form *S,S*-dimethyl-*N*-*p*-toluenesulfonylsulfilimine (**4**), which was isolated in crystalline form in 77% yield without necessity of chromatography. Sulfonylsulfilimines[7] of this type are fairly well-known compounds that have been prepared by the reactions of sulfonylnitrenes[8] with dialkyl sulfides. The nitrenes can be generated *via* either α elimination of chloride ion from salts of *N*-chlorosulfonamides (*e.g.*, chloramine-T)[9] or by photolysis of sulfonylazides.[10] Alternatively, sulfonylsulfilimines have been prepared by the reactions of sulfonamides with DMSO in the presence of either phosphorus pentoxide or acetic anhydride[11] and by the reaction of sulfonyl iso-

(1) For part XI, see U. Lerch and J. G. Moffatt, *J. Org. Chem.*, **36**, 3391 (1971).

(2) Syntex postdoctoral Fellow, 1966–1968.

(3) (a) K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 5661, 5670 (1965); (b) for a review, see J. G. Moffatt in "Techniques and Applications in Organic Synthesis: Oxidation," Vol. 2, R. Augustine and D. J. Trecker, Ed., Marcel Dekker, New York, N. Y., 1971.

(4) (a) M. G. Burdon and J. G. Moffatt, *J. Amer. Chem. Soc.*, **88**, 5855 (1966); (b) *ibid.*, **89**, 4725 (1967).

(5) A. F. Cook and J. G. Moffatt, *ibid.*, **90**, 740 (1968).

(6) A. H. Fenselau, E. H. Hamamura, and J. G. Moffatt, *J. Org. Chem.*, **35**, 3546 (1970).

(7) For a review on sulfilimines, see F. Challanger in "Organic Sulfur Compounds," Vol. 2, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, p 339.

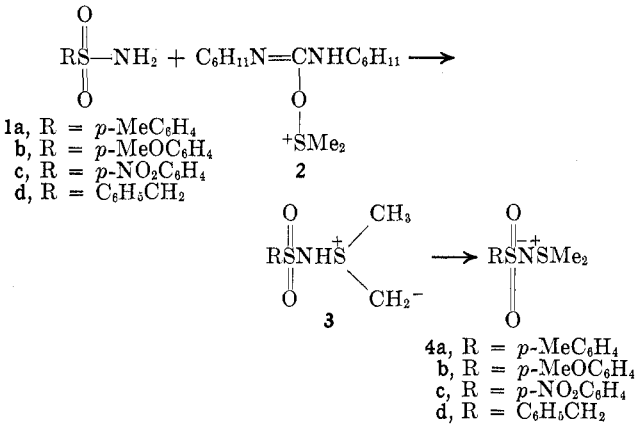
(8) D. S. Breslow in "Nitrenes," W. Lwowski, Ed., Interscience Publishers, New York, N. Y., 1970, p 245.

(9) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, 1052 (1922).

(10) (a) L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963); (b) L. Horner, G. Bauer, and J. Dourges, *ibid.*, **98**, 2631 (1965).

(11) D. S. Tarbell and C. Weaver, *J. Amer. Chem. Soc.*, **63**, 2939 (1941).

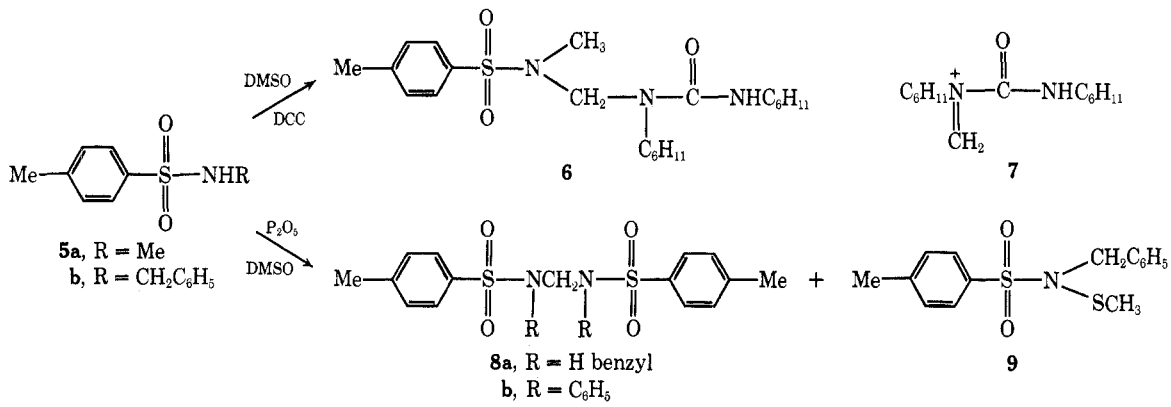
cyanates with sulfoxides.[12] In the present case, the formation of **4** doubtless involves direct attack of the amide nitrogen of **1** upon the DMSO–DCC adduct (**2**) to give the sulfonium ylide (**3**) which then undergoes a prototropic shift to form the more stable sulfilimine (**4**).



In this sequence we assume that the ylide **3** is the direct product of the condensation of **1** and **2** by an intramolecular proton abstraction mechanism similar to that we have proposed for the oxidation of alcohols.[13] If indeed this does not apply, then the direct product from reaction of **1** and **2** would be protonated form of **4**, which could then readily lose a proton to form the sulfilimine. Similar reactions between *p*-methoxybenzenesulfonamide (**1b**) and *p*-nitrobenzenesulfonamide (**1c**) and DMSO–DCC led to the formation of the corresponding sulfilimines (**4b** and **4c**)[10] in yields of 66 and 90%. The case of **1c** provides a clear example of a reaction in which DCC is not the preferred carbodiimide. The sulfilimine (**4c**) is extremely insoluble and crystallizes from the reaction mixture with dicyclohexylurea when DCC is used. By using diisopropylcarbodiimide the resulting diisopropylurea is quite soluble in many organic solvents and pure **4c** can be isolated in 90% yield by direct crystallization from methanol. On the other hand, the ylides **4a** and **4b** are soluble in water but can be conveniently recovered from the aqueous extracts during the usual reaction work-up by extraction into chloroform. In all three cases, the yields of sulfilimines are much higher than those obtained by photolysis of the sulfonylazides in dimethyl sulfide.[10] The sulfilimines **4a** and **4c** have also been obtained in yields of 17 and 44% by the mechanistically related acid-catalyzed reaction of the corresponding sulfonamides with DMSO and phenyl cyanate at 100°.[14] As an example of an aliphatic sulfonamide, the reaction of toluene-α-sulfonamide (**1d**) gave the corresponding sulfilimine (**4d**) in 70% yield.

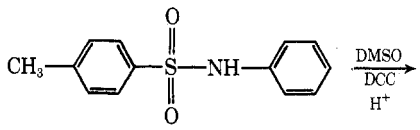
Photolysis of the related *N*-benzoylsulfilimines in methanol was previously shown to proceed *via* formation of the *N*-acylnitrene which reacted with the solvent or rearranged to an isocyanate.[1] Similar irradiation of a methanolic solution of **4a**, however, gave 26% ammonium *p*-toluenesulfonate, 17% *p*-toluenesulfonamide, and at least five other minor products that have not been identified.

Simple aliphatic substitution of the sulfonamide nitrogen as in *N*-methyl-*p*-toluenesulfonamide (**5a**) of course blocks the formation of sulfilimines. A very slow reaction does occur between **5a**, DMSO, and DCC, but even after 10 days 57% of unreacted **5a** was recovered. The only isolable new product was shown to be *N*-methyl-*N*-(1,3-dicyclohexyl-1-ureidomethyl)-*p*-toluenesulfonamide (**6**), which presumably arises from reaction of the amide with a species such as **7** as proposed previously for other slow reactions.[1] On the other hand, *N*-benzyl-*p*-toluenesulfonamide (**5b**) reacted fairly readily with DMSO in the presence of phosphorus pentoxide at room temperature, giving *N*,*N*′-methylenebis(*N*-benzyl-*p*-toluenesulfonamide) (**8a**) in 58% yield. The formation of methylene bisamides has previously been reported by Sekera and Rumpf[15] during reactions of N-substituted sulfonamides with DMSO and phosphorus pentoxide at 150°. These authors have proposed a mechanism for this reaction involving an *N*-alkyl derivative of the ylide (**3**) as an intermediate but this has been questioned by Martin, *et al.*[16] An alternative possibility is the direct condensation of the sulfonamide with formaldehyde generated by decomposition of DMSO.[1] We have previously described the formation of methylene bisamides upon reaction at room temperature of carboxylic acid amides with DMSO and phosphorus pentoxide while the corresponding reactions using DCC gave *N*-acylsulfilimines.[1] A second crystalline product was also isolated in 7% yield from the reaction of **5b** with DMSO and phosphorus pentoxide and shown by elemental analysis and nmr spectroscopy to be *N*-benzyl-*N*-methylthio-*p*-toluenesulfonamide (**9**). This compound presumably arises by nucleophilic demethylation of an intermediate *N*-dimethylsulfonium derivative by reaction with phosphate anion or perhaps even DMSO.



(12) C. King, *J. Org. Chem.*, **25**, 352 (1960).
(13) J. G. Moffatt, *ibid.*, **36**, 1909 (1971).
(14) D. Martin and H.-J. Niclas, *Chem. Ber.*, **102**, 31 (1969).
(15) A. Sekera and P. Rumpf, *C. R. Acad. Sci.*, **260**, 2252 (1965).
(16) D. Martin, H.-J. Niclas, and A. Weise, *Chem. Ber.*, **102**, 23 (1969).

The presence of an aromatic substituent on the sulfonamide nitrogen led to different results. Thus, the reaction of *p*-toluenesulfonanilide (**10**) under the usual



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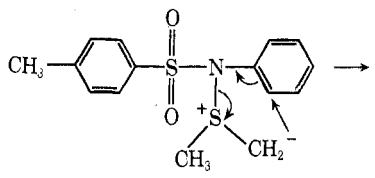

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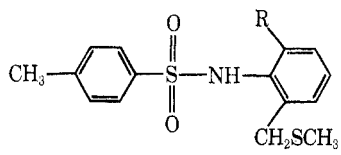
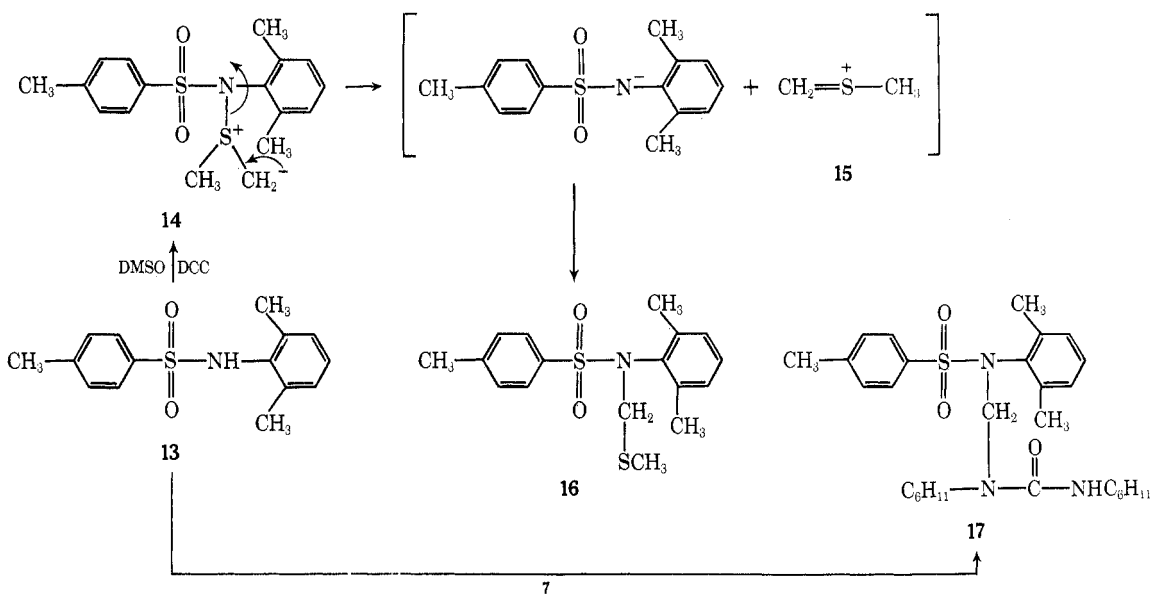


12a, R = H
b, R = CH_2SCH_3

conditions led to the isolation of two compounds **12a** (24%) and **12b** (27%) in which methylthiomethyl groups were introduced in one or both of the available ortho positions of the aromatic ring. This result is very reminiscent of what was previously described for the reactions of phenols with DMSO and DCC[4] *via* an intramolecular ortho alkylation reaction originating from the initially formed sulfonium ylide (**11**). The dialkylated product (**12b**) is, of course, the result of a second reaction of **12a** with DMSO and DCC in the same way. The structures of **12a** and **12b** were unequivocally confirmed by their ready desulfurization with nickel to the known *p*-toluenesulfono-*o*-toluidide[17] and *p*-toluenesulfono-2′,6′-xylidide.[18]

As was found in other cases, the reaction of **10** with DMSO and phosphorus pentoxide took a different course and gave *N*,*N*′-methylenebis-*p*-toluenesulfonanilide (**8b**) in 66% yield. The latter compound was readily identified by its elemental analysis and its nmr spectrum which showed the methylene bridge as a 2-proton singlet at 5.58 ppm.

It was previously shown that the reactions of 2,6-disubstituted phenols, such as 2,6-dimethylphenol, with DMSO and DCC led to the formation of 6-methylthiomethylcyclohexa-2,4-dien-1-ones. The latter compounds were shown to readily rearrange to the corresponding 4-methylthiomethylphenols under acidic conditions, the reaction proceeding by dissociation of the dienone into the methylmethylenesulfonium ion which then alkylated the para position of the released phenol.[4b] In order to see whether a similar reaction would occur in the sulfonanilide series, *p*-toluenesulfono-2′,6′-xylidide (**13**)[18] was treated with DMSO and DCC. A slow reaction occurred from which it was possible to isolate two crystalline products in yields of 21 and 25% in addition to 49% of unreacted **13**. These proved to be the N-substituted derivatives *N*-methylthiomethyl-*N*-*p*-toluenesulfonyl-2,6-xylidine (**16**) and *N*-(1,3-dicyclohexyl-1-ureidomethyl)-*N*-*p*-toluenesulfonyl-2,6-xylidine (**17**), the structures being readily apparent from their nmr spectra. It thus appears that the initial sulfonium ylide (**14**) show little, if any, tendency toward intramolecular alkylation of the xylidine moiety but rather dissociates into the anion of the starting material (**13**) and the methyl methylenesulfonium ion (**15**). Recombination of the latter species then gives the *N*-methylthiomethyl derivative (**16**). The urea derivative (**17**) once again is probably derived from a species such as **7**.

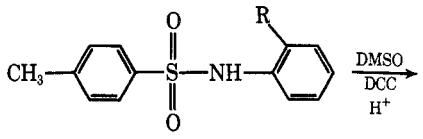


14 **15** **13** **16** **17** **7**

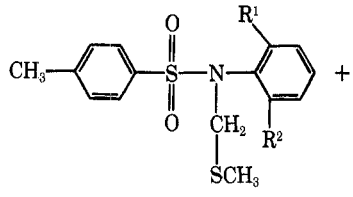
An attempt to prepare *N*-*p*-toluenesulfonyl-2,6-dichloroaniline failed, since the reaction of 2,6-dichloroaniline with a slight excess of *p*-toluenesulfonyl chloride led instead to *N*,*N*-di-*p*-toluenesulfonyl-2,6-dichloroaniline, which was isolated in 67% yield.

In those cases where there is still a single, unsubstituted ortho position on the aniline ring, both nitrogen alkylation and aromatic substitution take place. Thus, the reaction of *N*-(2-cyanophenyl)-*p*-toluenesulfonamide (**18a**) with DMSO and DCC gave as its major product the *N*-methylthiomethyl derivative (**19a**, 47%) in addition to smaller amounts of aromatic ortho alkylation product (**20**, 9%) and the bismethylthiomethyl compound **19b** (22%). In a similar way the reaction

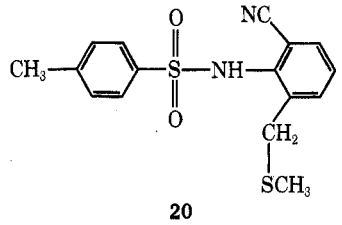
(17) F. D. Chattaway, *J. Chem. Soc.*, **85**, 1186 (1901).
(18) B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **73**, 809 (1954).



18a, R = CN
b, R = NO_2



19a, R^1 = CN; R^2 = H
b, R^1 = CN; R^2 = CH_2SCH_3
c, R^1 = NO_2; R^2 = H
d, R^1 = NO_2; R^2 = CH_2SCH_3

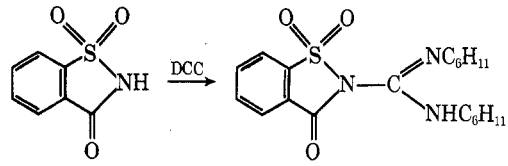


20

of *N*-(2-nitrophenyl)-*p*-toluenesulfonamide (**18b**) gave 54% of *N*-(methylthiomethyl)-*N*-(2-nitrophenyl)-*p*-toluenesulfonamide (**19c**) and 8% of the product (**19d**) alkylated on both nitrogen and the aromatic ring. In the case of the compound **19d** it is clear from the nmr spectrum that the methylthiomethyl group on the aromatic ring is indeed situated ortho to the amide function. Thus one aromatic proton, almost certainly that adjacent to the nitro group, is located at distinctly lower field than the others and appears as a quartet (J_{ortho} = 7 Hz, J_{meta} = 2 Hz) at 7.99 ppm. No orientation of the methylthiomethyl group other than that in **19e** permits this proton to have both ortho and meta neighbors. A similar orientation for **19b** and **19d** is expected on mechanistic grounds (*cf.* **12a**, **12b**, **19d**) but has not been rigorously proved. The nmr spectra of the doubly alkylated compounds (**19b** and **19d**) are also interesting in that the NCH_2S protons are nonequivalent and appear as AB quartets (J_{gem} = 14 Hz) centered at 4.91 and 4.95 ppm, respectively. This is undoubtedly a consequence of restricted rotation and is not observed in less substituted molecules where these protons appear as singlets. In the case of the nitro compound (**19d**), but not the nitrile (**19b**), the $ArCH_2$ group is also nonequivalent and appears as an AB quartet.

Finally, it might be mentioned that attempts to react saccharin (**21**) with DMSO and DCC failed to proceed in the desired way. Rather than reacting with the DMSO–DCC adduct (**2**), this very acidic sulfonamide added directly to DCC, giving, in essentially quantitative yield, a 1:1 adduct considered to be the guanidine (**22**). This same product was obtained in 93% yield by reaction of **21** and DCC in ethyl acetate. It is presumably the same material briefly described by Micheel and Lorenz,[19] although the melting point reported by these authors is 10° lower than that found by us.

(19) F. Micheel and M. Lorenz, *Justus Liebigs Ann. Chem.*, **698**, 242 (1966).



21 **22**

Subsequent papers in this series will describe the reactions of further types of nitrogenous functional groups with the DMSO–DCC reagent.[20]

Experimental Section

General experimental methods are as previously described.[1]

***S*,*S*-Dimethyl-*N*-*p*-toluenesulfonylsulfilimine (4a).**—A solution of anhydrous orthophosphoric acid in DMSO (1.6 ml of 3 *M*, 5 mmol) was added to a solution of *p*-toluenesulfonamide (1.71 g, 10 mmol) and DCC (6.18 g, 30 mmol) in DMSO (10 ml) and benzene (5 ml). After 2 days at 23° the mixture was diluted with ethyl acetate, dicyclohexylurea was removed by filtration, and the filtrate was extracted four times with water. The combined aqueous extracts were then repeatedly extracted (five times) with chloroform until tlc (chloroform–methanol, 9:1) showed complete removal of **4a**. The chloroform extracts were dried ($MgSO_4$) and evaporated, leaving a crystalline residue that was recrystallized from ethanol, giving 1.78 g (77%) of **4a** as long needles: mp 158–159° (lit.[10a] mp 158–159°); λ_{max}^{MeOH} 230 mμ (ε 11,330); ν_{max} (KBr) 1635 and 1580 cm^{-1}; nmr (DMSO-d_6) 2.37 (s, 3, $ArCH_3$), 2.69 (s, 6, SMe_2), 7.38 and 7.74 ppm (d, 2, *J* = 8 Hz, Ar); mass spectrum (70 eV) *m/e* 231 (M^+), 216 (M − CH_3) 167 (M − SO_2), 155 (M − Me_2SN), 152, 124 (Me_2SNSO).

Anal. Calcd for $C_9H_{13}NO_2S_2$: C, 46.75; H, 5.67; N, 6.06; S, 27.27. Found: C, 46.78; H, 6.14; N, 6.10; S, 27.57.

***S*,*S*-Dimethyl-*N*-*p*-methoxybenzenesulfonylsulfilimine (4b).**—A reaction between *p*-methoxybenzenesulfonamide (1.87 g, 10 mmol), DCC (6.18 g, 30 mmol), and anhydrous phosphoric acid (5 mmol) in DMSO (10 ml) and benzene (5 ml) was carried out exactly as above except that several further extractions with chloroform were necessary to remove the product from the aqueous phase. Crystallization of the final residue from ethanol (15 ml) gave 1.62 g (66%) of **4b**: mp 138.5–139.5°; λ_{max}^{MeOH} 239 mμ (ε 17,000); ν_{max} (KBr) 1600, 1580, 1495 cm^{-1}; nmr ($CDCl_3$) 2.67 (s, 6, SMe_2), 3.85 (s, 3, OMe), 6.93 and 7.84 ppm (d, 2, *J* = 9 Hz, Ar); mass spectrum (70 eV) *m/e* 247 (M^+), 232 (M − CH_3), 183 (M − SO_2), 171 ($MeOC_6H_4SO_2$), 168, 124 (Me_2SNSO).

Anal. Calcd for $C_9H_{13}NO_3S_2$: C, 43.73; H, 5.30; N, 5.67. Found: C, 43.78; H, 5.25; N, 5.46.

***S*,*S*-Dimethyl-*N*-*p*-nitrobenzenesulfonylsulfilimine (4c).**—Anhydrous phosphoric acid (5 mmol) was added to a solution of *p*-nitrobenzenesulfonamide (2.02 g, 10 mmol) and diisopropylcarbodiimide (3.78 g, 30 mmol) in DMSO (10 ml) and benzene (5 ml). After 16 hr the mixture was diluted with ethyl acetate and filtered. The resulting crystals were washed with ethyl acetate, dried (3.5 g), and crystallized from ethanol giving 2.36 g (90%) of pure **4c**: mp 186–187° (lit.[10a] mp 184°); λ_{max}^{MeOH} 271 mμ (ε 10,400); ν_{max} (KBr) 1610, 1530, 1355, 1285 cm^{-1}; nmr (DMSO-d_6) 2.73 (s, 6, SMe_2), 7.98 and 8.38 ppm (d, 2, *J* = 8 Hz, Ar); mass spectrum *m/e* 262 (M^+), 247 (M − CH_3), 198 (M − SO_2), 183 (*m/e* 198 − CH_3), 122 ($C_6H_4NO_2$), 76 (Me_2SN), 62 (Me_2S).

Anal. Calcd for $C_8H_{10}N_2O_4S_2$: C, 36.65; H, 3.84; N, 10.69. Found: C, 36.40; H, 3.74; N, 10.62.

***S*,*S*-Dimethyl-*N*-α-toluenesulfonylsulfilimine (4d).**—A solution of α-toluenesulfonamide (1.71 g, 10 mmol), DCC (6.18 g, 30 mmol), and anhydrous phosphoric acid (5 mmol) in DMSO (10 ml) and benzene (5 ml) was kept at 23° for 3 days. The mixture was then diluted with ethyl acetate and worked up as for **4a**. Crystallization of the chloroform-soluble product from ethanol gave 1.61 g (70%) of **4d** as needles: mp 147–148°; λ_{max}^{MeOH} 210 mμ (ε 9400), 215 (9100), 359 (200); ν_{max} (KBr) 1490, 1270 cm^{-1}; nmr ($CDCl_3$) 2.40 (s, 6, SMe_2), 4.25 (s, 2, $ArCH_2SO_2$), 7.45 (s, 5, Ar); mass spectrum (70 eV) *m/e* 231 (M^+), 167 (M − SO_2), 140 (Me_2SNSO_2), 91 ($C_6H_5CH_2$).

(20) U. Lerch and J. G. Moffatt, *J. Org. Chem.* in press.

Anal. Calcd for $C_9H_{13}NO_2S_2$: C, 46.75; H, 5.67; N, 6.06. Found: C, 46.63; H, 5.70; N, 5.85.

Photolysis of *S,S*-Dimethyl-*N*-*p*-toluenesulfonylsulfilimine (4a).—A solution of **4a** (1.16 g, 5 mmol) in methanol (90 ml) was irradiated for 19 hr in a quartz tube under argon using a 15W General Electric G 15T8 germicidal lamp. Some insoluble material was removed and the filtrate was evaporated and crystallized from chloroform–methanol giving 247 mg (26%) of ammonium *p*-toluenesulfonate which melted with decomposition at 250–280°: λ_{max}^{MeOH} 222 mμ (ε 11,400); nmr (DMSO-d_6), 2.29 (s, 3, $ArCH_3$), 7.17 and 7.60 (d, 2, J = 8 Hz, Ar), 7.2 ppm (br s, 4, NH_4).

Anal. Calcd for $C_7H_{11}NO_3S$: C, 44.41; H, 5.86; N, 7.40. Found: C, 44.21; H, 6.38; N, 7.35.

Preparative tlc (ethyl acetate–methanol, 5:1) of the mother liquors gave 41 mg (4%) of unreacted **4a**, 141 mg (17%) of *p*-toluenesulfonamide, and at least five other unidentified, minor products.

Reaction of *N*-Methyl-*p*-toluenesulfonamide (5a).—A solution of **5a** (1.85 g, 10 mmol), DCC (5.8 g, 28 mmol), and anhydrous phosphoric acid (5 mmol) in DMSO (5 ml) and benzene (5 ml) was allowed to react for 10 days. Following the usual work-up with ethyl acetate the product was purified by preparative tlc using CCl_4–acetone (85:15) giving 1.05 g (57%) of unreacted **5a** and 670 mg (16%) of *N*-methyl-*N*-(1,3-dicyclohexyl-1-ureidomethyl)-*p*-toluenesulfonamide (**6**): mp 134–136° from ether; λ_{max}^{MeOH} 230 mμ (ε 13,700); ν_{max} (KBr) 1645 and 1530 cm^{-1}; nmr ($CDCl_3$) 0.8–2.1 (m, 20, cyclohexyl), 2.45 (s, 3, $ArCH_3$), 2.69 (s, 3, NCH_3), 3.7 (m, 2, >CHN), 4.54 (s, 2, NCH_2N), 5.25 (m, 1, NH), 7.36 (d, 2, J = 8 Hz, Ar), 7.70 ppm (d, 2, J = 8 Hz, Ar).

Anal. Calcd for $C_{22}H_{35}N_3O_3S$: C, 62.67; H, 8.37; N, 9.97; S, 7.61. Found: C, 62.74; H, 8.19; N, 9.92; S, 7.81.

Reaction of *N*-Benzyl-*p*-toluenesulfonamide (5b) with DMSO–Phosphorus Pentoxide.—After addition of **5b** (2.6 g, 10 mmol) to a premixed solution of P_2O_5 (1.7 g) in DMSO (15 ml) the mixture was kept for 48 hr at 23°, and the crystalline product was removed by filtration and washed with ether, giving 1.55 g (58%) of *N,N'*-methylenebis(*N*-benzyl-*p*-toluenesulfonamide) (**8a**): mp 196–197° (unchanged upon recrystallization from benzene); $\lambda_{max}^{dioxane}$ 2.30 mμ (ε 22,100); nmr ($CDCl_3$) 2.37 (s, 6, $ArCH_3$), 4.43 (s, 4, $ArCH_2N$), 4.87 (s, 2, NCH_2N), 7.2 ppm (m, 18, Ar).

Anal. Calcd for $C_{29}H_{30}N_2O_4S_2$: C, 65.14; H, 5.66; N, 5.24; S, 11.99. Found: C, 65.32; H, 6.12; N, 5.07; S, 11.87.

The mother liquors were worked up as usual and purified by preparative tlc using CCl_4–acetone (9:1), giving 465 mg (18%) of unreacted **5b** and 221 mg (7.2%) of *N*-benzyl-*N*-methylthio-*p*-toluenesulfonamide (**9**): mp 77–86° (from hexane, unchanged by repeated crystallization); λ_{max}^{MeOH} 230 mμ (ε 14,600); ν_{max} (KBr) 1600 and 1500 cm^{-1}; nmr ($CDCl_3$) 2.10 (s, 3, SMe), 2.35 (s, 3, $ArCH_3$), 4.55 (s, 2, $ArCH_2N$), 7.1–7.9 ppm (m, 9, Ar); mass spectrum (70 eV) m/e 307 (M^+), 259 (M − CH_3SH), 155 ($CH_3C_6H_4SO_2$), 150, 105, 91.

Anal. Calcd for $C_{15}H_{17}NO_2S_2$: C, 58.60; H, 5.57; N, 4.56; S, 20.86. Found: C, 58.77; H, 5.62; N, 4.39; S, 20.63.

Reaction with *p*-Toluenesulfonanilide (10). A. With DMSO–DCC.—A solution of **10** (2.45 g, 10 mmol), DCC (6.18 g, 30 mmol), and anhydrous phosphoric acid (5 mmol) in DMSO (10 ml) and benzene (5 ml) was allowed to react for 3 days at 23° and then worked up with ethyl acetate. Preparative tlc on three plates using two developments with CCl_4–acetone (9:1) gave 720 mg (29%) of unreacted **10** and two faster bands. The faster band gave only 240 mg of an oil that decomposed upon attempted distillation. Rechromatography of the slower band separated two compounds, the slower of which was crystallized from hexane giving 740 mg (24%) of 2-methylthiomethyl-*N*-*p*-toluenesulfonylaniline (**12a**): mp 93–95°; λ_{max}^{MeOH} 220 mμ (sh, ε 17,900); ν_{max} (KBr) 3300, 1610, 1500 cm^{-1}; nmr ($CDCl_3$) 1.81 (s, 3, SMe), 2.32 (s, 3, $ArCH_3$), 3.37 (s, 2, $ArCH_2S$), 7.4 ppm (m, 9, Ar and NH); mass spectrum (70 eV) m/e 307 (M^+), 196, 181, 152 (M − $MeC_6H_4SO_2$), 136 (M − $MeC_6H_4SO_2NH_2$).

Anal. Calcd for $C_{15}H_{17}NO_2S_2$: C, 58.60; H, 5.57; N, 4.56; S, 20.86. Found: C, 58.84; H, 5.55; N, 4.48; S, 21.06.

The faster portion was crystallized from hexane giving 990 mg (27%) of 2,6-di(methylthiomethyl)-*N*-*p*-toluenesulfonylaniline (**12b**): mp 89.5–91°; λ_{max}^{MeOH} only end absorption; ν_{max} (KBr) 3280, 1600, 1460, 1435 cm^{-1}; nmr ($CDCl_3$) 1.85 (s, 6, SMe), 2.41 (s, 3, $ArCH_3$), 3.49 (s, 4, $ArCH_2S$), 7.3 ppm (m, 8, Ar and NH).

Anal. Calcd for $C_{17}H_{21}NO_2S_2$: C, 55.55; H, 5.76; N, 3.81; S, 26.17. Found: C, 55.68; H, 5.54; N, 3.85; S, 26.29.

B. With DMSO–Phosphorus Pentoxide.—Phosphorus pentoxide (2.5 g) was added gradually to DMSO (20 ml) and cooled to room temperature. *p*-Toluenesulfonanilide (3.61 g, 15 mmol) was then added and the mixture was stirred at 23° for 20 hr. Since much unreacted **10** was still present, the mixture was heated to 70° for 4 hr. Upon cooling, crystalline *N,N'*-methylenebis-*p*-toluenesulfonanilide (**8b**, 945 mg) separated: mp 212–214°; λ_{max}^{MeOH} 233 mμ (ε 2800); ν_{max} 1600, and 1495 cm^{-1}; nmr ($CDCl_3$) 2.36 (s, 6, $ArCH_3$), 5.58 (s, 2, NCH_2N), 7.2 ppm (m, 18, Ar); mass spectrum (70 eV) m/e 260 (M − TsNAr), 247 (TsNAr), 155 ($MeC_6H_4SO_2$).

Anal. Calcd for $C_{27}H_{26}N_2O_4S_2$: C, 63.75; H, 5.55; N, 5.51; S, 12.61. Found: C, 63.91; H, 5.26; N, 5.69; S, 12.75.

The mother liquors were extracted three times with water, dried, and purified by preparative tlc using benzene–ethyl acetate (19:1) giving only 653 mg (18%) of unreacted **10** and 1.59 g (total yield 2.52 g, 66%) of **8b**.

Desulfurization of 12a and 12b.—A solution of **12b** (175 mg) in methanol (5 ml) was stirred for 3 hr with about 2 g of Davidson sponge nickel.[21] The mixture was then filtered and evaporated, leaving 111 mg (84%) of crystalline *p*-toluenesulfono-2',6'-xylidide, mp 135–137° from benzene–hexane (lit.[18] mp 136.5–137.5°). This material was identical with an authentic sample by infrared spectra, tlc, and mixture melting point.

Identical treatment of **12a** (105 mg) for 45 min gave 84 mg (97%) of *p*-toluenesulfono-*o*-toluidide, mp 108–109°, that was identical with an authentic sample.[17]

Reaction of *p*-Toluenesulfono-2',6'-xylidide (13).—A solution of **13** (2.75 g, 10 mmol),[18] DCC (5.8 g), and anhydrous phosphoric acid (5 mmol) in DMSO (5 ml) and benzene (5 ml) was kept at 23° while the reaction was followed by tlc using CCl_4–acetone (9:1). After 8 days it was worked up using ethyl acetate and separated on four preparative tlc plates (9:1 CCl_4–acetone), giving two major bands. Elution of the fastest band gave 712 mg (21%) of crystalline *N*-methylthiomethyl-*N*-*p*-toluenesulfonyl-2,6-xylidine (**16**): mp 128–130° from hexane; λ_{max}^{MeOH} 234 mμ (sh, ε 11,000), 276 (1300); ν_{max} (KBr) 1600, 1470, 1340 cm^{-1}; nmr ($CDCl_3$) 2.11 (s, 6, $ArMe_2$), 2.18 (s, 3, SMe), 2.45 (s, 3, $ArCH_3$), 4.79 (s, 2, NCH_2S), 7.2–7.8 ppm (m, 7, Ar).

Anal. Calcd for $C_{17}H_{21}NO_2S_2$: C, 60.86; H, 6.31; N, 4.18; S, 19.11. Found: C, 60.89; H, 6.27; N, 4.34; S, 19.37.

Rechromatography of the slower band using CCl_4–acetone (87:13) separated it into two bands, the slower of which contained 1.34 g (49%) of unreacted **13**. Crystallization of the faster band from methanol gave 1.28 g (25%) of *N*-(1,3-dicyclohexyl-1-ureidomethyl)-*N*-*p*-toluenesulfonyl-2,6-xylidine (**17**): mp 158–195°; λ_{max}^{MeOH} 233 mμ (ε 12,800), 264 (1800), 276 (ε 1100); ν_{max} (KBr) 3400, 1660, 1535 cm^{-1}; nmr ($CDCl_3$), 1–2.2 (m, 20, cyclohexyl), 2.85 (s, 6, $ArMe_2$), 2.42 (s, 3, ArMe), 3.50 (m, 2, CHN), 5.00 (s, 2, NCH_2N), 6.56 (d, 1, J = 8 Hz, NH), 7.1–7.7 ppm (m, 7, Ar).

Anal. Calcd for $C_{29}H_{41}N_3O_3S$: C, 68.07; H, 8.08; N, 8.21; S, 6.27. Found: C, 68.04; H, 8.20; N, 8.11; S, 6.40.

***N*-(2-Cyanophenyl)-*p*-toluenesulfonamide (18a).**—Anthranilonitrile and *p*-toluenesulfonyl chloride (1.1 equiv) were allowed to react in pyridine at 100° for 5 hr. The mixture was then poured into water and the precipitate was crystallized from methanol, giving **18a** in 87% yield: mp 138–139°; λ_{max}^{MeOH} 209 mμ (ε 31,400), 220 (sh, 22,800); nmr ($CDCl_3$) 2.37 (s, 3, ArMe), 7.5 ppm (m, 9, Ar and NH).

Anal. Calcd for $C_{14}H_{12}N_2O_2S$: C, 61.74; H, 4.44; N, 10.29; S, 11.78. Found: C, 61.75; H, 4.44; N, 10.16; S, 11.89.

Reaction of *N*-(2-Cyanophenyl)-*p*-toluenesulfonamide (18a).—A solution of **18a** (2.72 g, 10 mmol), DCC (5.8 g), and anhydrous phosphoric acid (5 mmol) in DMSO (5 ml) and benzene (5 ml) was kept for 2 days and worked up with ethyl acetate. The extracted organic phase was chromatographed on four plates using CCl_4–acetone (85:15), giving three bands. Elution of the fastest band gave 878 mg (22%) of *N*-(2-cyano-6-methylthiomethylphenyl)-*N*-methylthiomethyl-*p*-toluenesulfonamide (**19b**): mp 101–102° from ether–hexane; λ_{max}^{MeOH} 222 mμ (sh, ε 23,700), 289 (sh, 1900); ν_{max} (KBr) 2240, 1610, 1585 cm^{-1}; nmr ($CDCl_3$) 2.03 (s, 3, SMe), 2.22 (s, 3, SMe), 2.42 (s, 3, ArMe), 3.82 (s, 2, $ArCH_2S$), 4.76 and 5.05 (d, 1, J_{gem} = 14 Hz, NCH_2S), 7.5 ppm (m, 7, Ar).

(21) Davidson Chemical Division of W. R. Grace & Co., Cincinnati, Ohio.

Anal. Calcd for $C_{18}H_{20}N_2O_2S_3$: C, 55.07; H, 5.14; N, 7.14; S, 24.50. Found: C, 54.64; H, 5.12; N, 6.87; S, 24.18.

Elution of the middle band and crystallization from ether gave 1.575 g (47%) of *N*-(2-cyanophenyl)-*N*-methylthiomethyl-*p*-toluenesulfonamide (**19a**): mp 97–98°; λ_{max}^{MeOH} 220 mμ (sh, ε 21,600), 276 (sh, 1700); ν_{max} (KBr) 2250, 1600, 1495 cm^{-1}; nmr ($CDCl_3$) 2.22 (s, 3, SMe), 2.37 (s, 3, ArMe), 4.70 (s, 2, NCH_2S), 7.4 ppm (m, 8, Ar); mass spectrum (70 eV) *m/e* 332 (M^+), 285 (M − SMe), 177 (M − $ArSO_2$), 155 ($MeC_6H_4SO_2$), 130 (*m/e* 177 − SMe).

Anal. Calcd for $C_{16}H_{16}N_2O_2S_2$: C, 57.81; H, 4.85; N, 8.43; S, 19.29. Found: C, 57.47; H, 5.22; N, 8.25; S, 19.32.

Rechromatography of the slowest band using five developments with CCl_4–acetone (82:18) separated 464 mg (17%) of unreacted **18a** from 293 mg (9%) of *N*-(2-cyano-6-methylthiomethylphenyl)-*p*-toluenesulfonamide (**20**): mp 125–128° from ether; λ_{max}^{MeOH} 222 mμ (sh, ε 28,200), 285 (sh, 1700); ν_{max} (KBr) 3300, 2240, 1635, 1600, 1585 cm^{-1}; nmr ($CDCl_3$) 1.89 (s, 3, SMe), 2.42 (s, 3, ArMe), 3.55 (s, 2, $ArCH_2S$), 7.5 ppm (m, 8, Ar and NH); mass spectrum (70 eV) *m/e* 332 (M^+), 177 (M − $MeC_6H_4SO_2$), 155 ($MeC_6H_4SO_2$), 131 (*m/e* 177 − SMe).

Anal. Calcd for $C_{16}H_{16}N_2O_2S_2$: C, 57.81; H, 4.85; N, 8.43; S, 19.29. Found: C, 57.83; H, 5.02; N, 8.25; S, 19.20.

Reaction of *N*-(2-Nitrophenyl)-*p*-toluenesulfonamide (18b).—A solution of **18b** (2.92 g, 10 mmol), DCC (6.18 g, 30 mmol), and anhydrous phosphoric acid (5 mmol) in DMSO (10 ml) and benzene (5 ml) was kept for 3 days at room temperature. After dilution with ether, filtration, and three extractions with water, the solution was extracted four times with 1 *N* sodium hydroxide. Acidification of the extracts and extraction with chloroform gave 0.79 g of relatively pure unreacted **18b**. Preparative tlc of the alkali insoluble fraction using three developments with hexane–ether (3:2) gave two products. Elution of the major, slower band gave 1.90 g (54%) of *N*-(2-nitrophenyl)-*N*-methylthiomethyl-*p*-toluenesulfonamide (**19c**) as a very viscous yellow syrup. An analytical sample could be distilled in a Kugelrohr apparatus[22] at 150° (10^{-3} mm): λ_{max}^{MeOH} 227 mμ (ε 17,400); ν_{max} (KBr) 1605, 1550, 1175 cm^{-1}; nmr ($CDCl_3$) 2.20 (s, 3, SMe), 2.41 (s, 3, ArMe), 4.87 (s, 2, NCH_2S), 7.1–7.9 ppm (m, 8, Ar).

Anal. Calcd for $C_{15}H_{16}N_2O_4S_2$: C, 51.14; H, 4.58; N, 7.95. Found: C, 51.47; H, 4.72; N, 7.71.

Elution of the faster and gave 355 mg (8%) of *N*-(methylthiomethyl)-*N*-(2-methylthiomethyl-6-nitrophenyl)-*p*-toluenesulfonamide (**19d**) as a viscous syrup: λ_{max}^{MeOH} 225 mμ (sh, ε 18,500); ν_{max} (KBr) 1600, 1535 cm^{-1}; nmr ($CDCl_3$) 2.12 (s, 3, SMe), 2.20 (s, 3, SMe), 2.42 (s, 3, ArMe), 3.77 and 4.15 (d, 1, J_{gem} = 14 Hz, $ArCH_2S$), 4.74 and 5.17 (d, 1, J_{gem} = 14 Hz, NCH_2S), 7.1–8 ppm (m, 7, Ar).

Anal. Calcd for $C_{17}H_{20}N_2O_4S_3$: C, 49.51; H, 4.89; N, 6.79. Found: C, 49.86; H, 4.97; N, 6.61.

***N*,*N*-Di-*p*-Toluenesulfonyl-2,6-dichloroaniline.**—A solution of 2,6-dichloroaniline (8.1 g, 50 mmol) and *p*-toluenesulfonyl chloride (10.0 g, 53 mmol) in pyridine (30 ml) was heated under reflux for 2 days. After evaporation of the solvent the residue was triturated with aqueous methanol (1:1) giving 7.8 g (67%) of *N*,*N*-di-*p*-toluenesulfonyl-2,6-dichloroaniline: mp 252–255° (raised to 256–258° upon recrystallization from chloroform–methanol); ν_{max} (KBr) 1600, 1570, 1495, 1440 cm^{-1}; nmr ($CDCl_3$) 2.46 (s, 6, ArMe), 7.32 (m, 7, Ar), 7.95 (d, 4, J = 8 Hz, Ar).

Anal. Calcd for $C_{20}H_{17}NO_4S_2Cl_2$: C, 51.07; H, 3.64; N, 2.98; S, 13.63. Found: C, 50.95; H, 3.67; N, 3.04; S, 13.64.

***N*-(1,3-Dicyclohexylformamidin-2-yl)saccharin (22).**—Saccharin (1.83 g, 10 mmol) and DCC (2.26 g, 11 mmol) were dissolved in ethyl acetate (5 ml) with gentle warming. After a few minutes crystals began to separate and after 16 hr the mixture was diluted with hexane and filtered. The crystals were washed with hexane and dried, leaving 4.0 g of **22** contaminated with only a trace of dicyclohexylurea. Recrystallization from methanol gave 3.62 g (93%) of pure **22**: mp 200–201°; λ_{max}^{MeOH} 225 mμ (ε 21,700); ν_{max} (KBr) 3310, 1665, 1570 cm^{-1}; nmr ($CDCl_3$) 0.9–2.5 (m, 20, cyclohexyl), 3.8 and 4.5 (m, 1, >CHN), 5.38 (d, 1, $J_{H,NH}$ = 7 NH), 7.5–8.0 ppm (m, 4, Ar); mass spectrum (70 eV) *m/e* 389 (M^+), 308 (M − C_6H_9), 226 (M − $2C_6H_9$), 206 (DCC^+), 183 (M − HDCC).

Anal. Calcd for $C_{20}H_{27}N_3O_3S$: C, 61.68; H, 6.99; N, 10.79. Found: C, 61.48; H, 7.05; N, 10.53.

Registry No.—**2**, 29494-72-2; **4a**, 31657-44-7; **4b**, 31657-42-8; **4c**, 31657-43-9; **4d**, 31657-44-0; **5a**, 640-61-9; **5b**, 1576-37-0; **6**, 31657-47-3; **8a**, 31657-48-4; **8b**, 1109-54-2; **9**, 31657-50-8; **10**, 68-34-8; **12a**, 31657-51-9; **12b**, 31657-52-0; **13**, 4703-15-5; **16**, 31657-54-2; **17**, 31657-55-3; **18a**, 31659-28-6; **18b**, 6380-13-8; **19a**, 31659-30-0; **19b**, 31659-31-1; **19c**, 31659-32-2; **19d**, 31659-33-3; **20**, 31659-34-4; **22**, 31659-33-5; ammonium *p*-toluenesulfonate, 4124-42-9; *N*,*N*-di-*p*-toluenesulfonyl-2,6-dichloroaniline, 31659-37-7; DMSO, 67-68-5.

(22) R. Graeve and G. H. Wahl, *J. Chem. Educ.*, **41**, 279 (1964).

Addition of Sulfonyl Chlorides to Acetylenes. I. Stereoselective Syntheses of β-Chlorovinyl Sulfones[1]

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The copper-catalyzed addition of sulfonyl chlorides to acetylenes makes possible the one-step syntheses of β-chlorovinyl sulfones in high yields. The stereoselective 1:1 addition apparently takes place by a free-radical chain reaction in which the copper catalyst functions as a chlorine atom transfer agent. The stereochemical course of the addition and configurational assignments of the isomeric adducts are discussed. Addition products of aryl-, methane-, and chloromethanesulfonyl chlorides and phenylacetylene, terminal alkynes (1-hexyne and 1-octyne), nonterminal alkyne (3-hexyne), and diphenylacetylene are described.

This paper presents examples of 1:1 additions of sulfonyl chlorides across the triple bond yielding β-chlorovinyl sulfones in high yields; these examples describe the addition of an arylsulfonyl chloride (R = C_6H_5) and alkylsulfonyl chlorides (R = CH_3, $ClCH_2$) to phenylacetylene, 1-hexyne, 1-octyne, and 3-hexyne, as well as the addition of *p*-toluenesulfonyl chloride to diphenylacetylene.[2]

$$RSO_2Cl + R'C{\equiv}CR'' \longrightarrow RSO_2CR'{=}CClR''$$

R = C_6H_5, *p*-$CH_3C_6H_4$, CH_3, ClCH

R′ = H, C_2H_5;

R″ = C_6H_5, C_2H_5, *n*-C_4H_9, *n*-C_6H_{13}

The known synthetic routes leading to β-chlorovinyl sulfones are usually based on at least two steps. Typically, step 1 involves (a) nucleophilic addition of a

(1) Presented before the Second Organic Sulphur Symposium, Groningen, The Netherlands, May 1966; Y. Amiel, *Tetrahedron Lett.*, 661 (1971).

(2) After this paper was submitted for publication, W. E. Truce, C. T. Goralski, L. W. Christensen, and R. H. Bavry, *J. Org. Chem.*, **35**, 4217 (1970), described the addition of benzenesulfonyl chloride to phenylacetylene, giving a monoadduct of an unknown configuration, whereas treatment of benzenesulfonyl chloride with diphenylacetylene resulted only in recovered diphenylacetylene.