added. Cyanogen chloride (5.2 g) was added in one portion and the mixture was stirred for 40 min. The mixture was filtered to remove the sodium chloride. The filtrate was evaporated to dryness. The residue was stirred with 20 ml of benzene and filtered to give 4.67 g of crude 11, mp 181–185°. Two recrystallizations from ethyl acetate gave 2-aza-4-cyano-1,1,1,5,5,5-hexaphenylpenta-2,3-diene (11), mp 200–202°.

Anal. Calcd for $C_{41}H_{30}N_2$: C, 89.4; H, 5.50; N, 5.08; mol wt, 551. Found: C, 89.4; H, 5.51; N, 5.00; mol wt, (ebullition in benzene), 563, 550.

The infrared spectrum of 11 showed absorption at 3.27 (unsaturated CH), 4.54 (conjugated nitrile), and 4.88 μ (cumulative unsaturation). The ultraviolet spectrum of 11 in acetonitrile showed λ_{max} 305 mμ (ϵ 782) and 250 mμ (ϵ 14,900).

The Reaction of Sulfonylureas and Sulfonamides with Carbonyl Chloride. A New Synthesis of Isocyanates[1]

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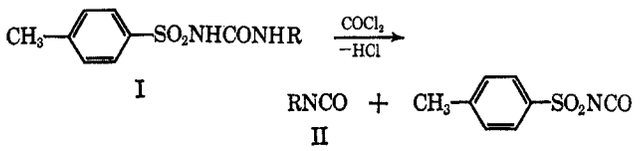
Received March 3, 1966

Several hitherto inaccessible mono- and diisocyanates were afforded from the reaction of carbonyl chloride with 1-arylsulfonyl-3-alkylureas and with alkylenebis(arylsulfonylureas) and -(sulfanilylureas), respectively. The conversion of arylsulfonamides to the corresponding arylsulfonyl isocyanates was readily accomplished by an isocyanate-catalyzed phosgenation reaction.

We recently reported that the reaction of 1,3-dialkylureas with carbonyl chloride affords a mixture of the N,N′-dialkylchloroformamidine hydrochlorides and the 2,4-dialkylallophanoyl chlorides,[2] the latter compounds being successfully dehydrochlorinated to alkyl isocyanates and alkylene diisocyanates.[3] In the case of the 1-arylsulfonyl-3-alkylureas, where the presence of the sulfonyl grouping can render the adjacent NH grouping less reactive to carbonyl chloride, one would expect both the arylsulfonyl and the alkyl isocyanates to be formed in good yield.

Further interest was provided by the sluggish reactions and poor yields reported for the reaction of sulfonamides with carbonyl chloride[4] and by the hope for obtaining alkylene diisocyanates and alkoxyethyl isocyanates from the 1-arylsulfonyl-3-alkylureas and alkylenebis(arylsulfonylureas), respectively—compounds obtainable only from the laborious Curtius degradation.[5]

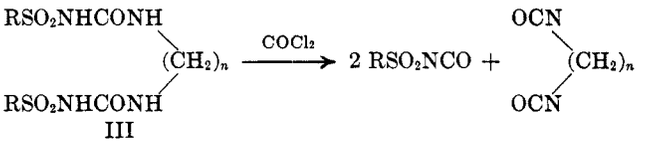
The model compound, 1-*p*-toluenesulfonyl-3-*n*-butylurea (Ia), on reaction with carbonyl chloride in chlorobenzene at temperatures above 80°, did afford *n*-butyl isocyanate (IIa) and *p*-toluenesulfonyl isocyanate in the excellent yields of 85.2 and 88.5%, respectively. The reaction would not take place at room temperature. Similarly, 1-*p*-toluenesulfonyl-3-(2-ethoxyethyl)urea (Ib) gave the novel 2-ethoxyethyl isocyanate (IIb) in 76% yield. That no ether cleavage accompanied the reaction was well evidenced by both vapor phase chromatographic and H^1 nmr spectroscopic data.



Ia, R = *n*-C_4H_9– IIa, R = *n*-C_4H_9–
b, R = $C_2H_5OCH_2CH_2$– b, R = $C_2H_5OCH_2CH_2$–

The several isocyanates prepared from 1-arylsulfonyl-3-alkylureas, along with their reaction conditions, are listed in Table I.

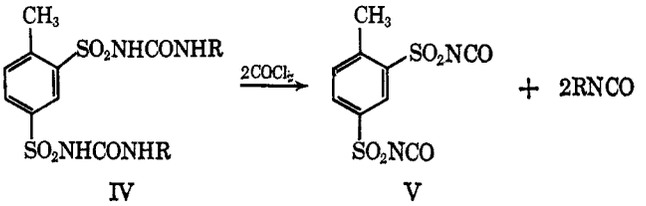
Bis(*p*-tolylsulfonylcarbamoyl)alkylenediamines (III), compounds readily available from the reaction of alkylenediamines with *p*-toluenesulfonyl isocyanate,[6] were also phosgenated, giving rise to the desirable alkylene diisocyanates listed in Table II.



III

R = *p*-CH_3C_6H

Similarly, the arylbis(sulfonylalkylureas) were phosgenated to aryldisulfonyl diisocyanates. N,N′-Bis(*n*-butylcarbamoyl)toluene-2,4-disulfonamide (IV), for example, was converted to toluene-2,4-disulfonyl diisocyanate (V, 38.3%).



IV V

R = *n*-butyl–

The success experienced with the carbonyl chloride-sulfonylurea reaction gave impetus to similar thoughts about the sulfanilylureas. Although the conversion of sulfanilamide to *p*-isocyanatobenzenesulfonamide was reported,[7,8] no syntheses for the isocyanatobenzenesulfonyl isocyanates appeared in the literature.[9] The large difference in reactivity of the isocyanato groupings renders these diisocyanates exceedingly useful in prepolymer systems.

(1) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(2) H. Ulrich, J. N. Tilley, and A. A. R. Sayigh, *J. Org. Chem.*, **29**, 2401 (1964).

(3) A. A. R. Sayigh, J. N. Tilley, and H. Ulrich, *ibid.*, **29**, 3344 (1964).

(4) H. Krzikalla, German Patent 817,602 (Oct. 18, 1951); *Chem. Abstr.*, **47**, 2206 (1953); C. King, *J. Org. Chem.*, **25**, 352 (1960); F. Effenberger and R. Gleiter, *Chem. Ber.*, **97**, 1576 (1964).

(5) W. Siefken, *Ann.*, **562**, 75 (1949).

(6) E. Habicht, U. S. Patent 2,962,530 (June 23, 1960); *Chem. Abstr.*, **55**, 17509 (1961).

(7) F. C. Meyer, U. S. Patent 2,827,470 (March 18, 1958); *Chem. Abstr.*, **52**, 12910 (1958); See also Houben-Weyl, "Methoden der Organischen Chemie IV," Vol. 8, Georg Thieme Verlag, Stuttgart, Germany, 1952, p 128.

(8) J. Smith, Jr., T. K. Brotherton, and J. W. Lynn, *J. Org. Chem.*, **30**, 1260 (1965).

(9) After completion of our work, Smith, Brotherton, and Lynn[8] reported the synthesis of one member of this class of compounds.

TABLE I

REACTION OF 1-ARYLSULFONYL-3-ALKYLUREAS WITH CARBONYL CHLORIDE

$$RSO_2NHCONHR' \longrightarrow RSO_2NCO + R'NCO$$

R	R'	Solvent	Temp, °C	% excess $COCl_2$	RSO_2NCO % yield	RSO_2NCO Bp, °C (mm)	R'NCO % yield	R'NCO Bp, °C
4-$CH_3C_6H_4$	n-C_4H_9	Chlorobenzene	130	50	88.8	100–106 (1.8)	85.2	115
4-$CH_3C_6H_4$	$C_2H_5OCH_2CH_2$	o-Dichlorobenzene	80–150	100	84.5	91–92 (0.5)	76	140–142[a]
4-$CH_3C_6H_4$	$CH_3OCH_2CH_2CH_2$	Toluene	115	200	84.5	91–93 (0.5)	70	143[b]
4-ClC_6H_4	n-C_3H_7	Chlorobenzene	130	100	57.9	94–95 (0.8)	70[c]	...

[a] The H^1 nmr spectrum [triplet, 1.15 ppm ($-CH_3$); multiplet, 3.4–3.5 ppm ($-CH_2$); ratio 3:6] demonstrated that no ether cleavage had occurred. [b] W. Siefken[5] obtained only impure material. No ether cleavage was evidenced by the H^1 nmr spectrum [singlet, 3.3 ppm ($-CH_3$); multiplet; 3.4 ppm; quartets, 1.8 ppm; ratio 3:4:2]. [c] Determined by titration with di-n-butylamine.[11]

TABLE II

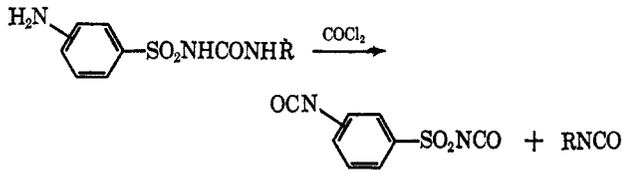
REACTION OF ALKYLENEBIS(ARYLSULFONYLUREAS) WITH CARBONYL CHLORIDE

$$p\text{-}CH_3C_6H_4SO_2NH\text{-}(CH_2)_n\text{-}NHSO_2C_6H_4CH_3\text{-}p \xrightarrow{2COCl_2} 2p\text{-}CH_3C_6H_4SO_2NCO + OCN\text{-}(CH_2)_n\text{-}NCO$$

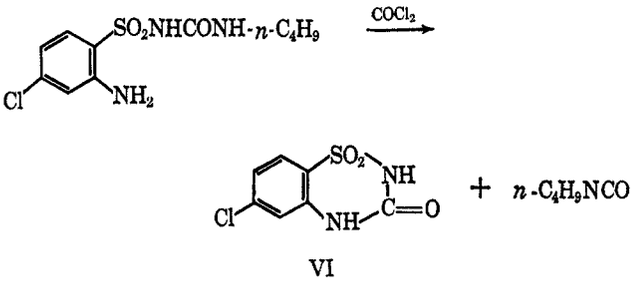
n	Solvent	Temp, °C	% excess $COCl_2$	$OCN(CH_2)_nNCO$, yield[a] %	p-$CH_3C_6H_4SO_2NCO$, yield[a] %
3	Chlorobenzene	127–130	50	40.0	75.6
4	Chlorobenzene	127–130	...[b]	62.7	70.8
4	o-Dichlorobenzene	170–180	200	75.0	78.0
6	o-Dichlorobenzene	130–140	...[b]	95.5	67

[a] Separation and yield determination of the alkylene diisocyanates and p-toluenesulfonyl isocyanate were accomplished with a vapor phase chromatograph, the separation being too difficult by fractional vacuum distillation. [b] Not determined.

Both the m- and p-sulfanilylureas, on phosgenation, afforded the corresponding isocyanatobenzenesulfonyl isocyanates in 45.7 and 64.3% yields, respectively.

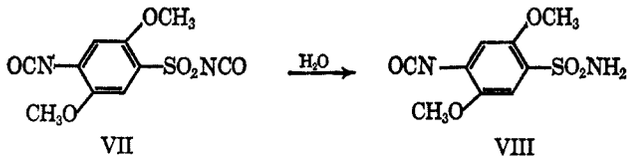


With the *ortho* isomer, ring closure to the benzothiadiazinone 1,1-dioxide (VI) occurred.



VI

The difference in isocyanato-group reactivity was apparent in the purification of 4-isocyanato-2,5-dimethoxybenzenesulfonyl isocyanate (VII) which was readily converted by atmospheric moisture to the sulfonamide (VIII).



VII VIII

The reported methods for the conversion of sulfonamides to sulfonyl isocyanates being poor,[4] our work was extended to include the development of a good, simple procedure. Two useful facts from the literature were that the high temperature reactions of carbonyl chloride with sulfonamides gave low yields of product[4] and that the mixture of products obtained from the oxalyl chloride–sulfonamide reaction contained arylsulfonyl isocyanates formed *via* a two-step reaction sequence.[10] These facts, in conjunction with our successful phosgenation of arylsulfonylureas at temperatures below 100°, made plausible a lower-temperature phosgenation of the sulfonamides in the presence of an isocyanate catalyst.

p-Toluenesulfonamide in chlorobenzene was treated at 130° with a small excess of carbonyl chloride and in the presence of a catalytic amount of n-butyl isocyanate to afford 92.5% of p-toluenesulfonyl isocyanate. The several isocyanates prepared from arylsulfonamides, along with reaction conditions and methylurethan derivatives for the new compounds, are listed in Table III. The low-boiling alkyl isocyanate could be recovered and reused.

The need for an alkyl or aryl isocyanate as catalysts was demonstrated in a model experiment in which phosgenation of p-toluenesulfonamide was attempted in the presence of 20% p-toluenesulfonyl isocyanate. No reaction was observed. In this two-step reaction the catalyst apparently converts the arylsulfonamide to the urea which in turn is phosgenated to the isocyanate. The formation of the urea being the rate-determining step, the amount of catalyst is not critical, although 20–40% will ensure a fast rate of reaction (*i.e.*, the reaction and addition rates of phosgene will be nearly equal). Low-boiling isocyanates gave the best results, the sterically hindered aliphatic isocyanates, such as cyclohexyl isocyanate, and aromatic isocyanates also working well. In the case of phenyl isocyanate, the first step is faster than with an alkyl isocyanate and the phosgenation of the less basic 1-

(10) J. E. Franz and C. Osuch, *J. Org. Chem.*, **29**, 2592 (1964).

TABLE III

REACTION OF ARYLSULFONAMIDES WITH CARBONYL CHLORIDE

$$RSO_2NH_2 \xrightarrow{COCl_2} RSO_2NCO + 2HCl$$

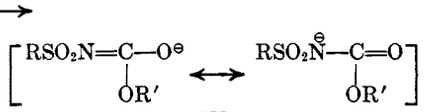
R	Solvent	Catalyst[a]	% excess $COCl_2$	% yield	Bp °C (mm) (mp, °C)	Methylurethan, $RSO_2NHCOOCH_3$: Mp °C	Empirical formula	Analysis, % Calcd	Found
C_6H_5	Chlorobenzene	*n*-C_4H_9NCO	50	85.8	79–83 (0.7)[b]				
4-$CH_3C_6H_4$	Chlorobenzene	*n*-C_4H_9NCO	30	92.5	91–92 (0.5)[c]				
4-$CH_3C_6H_4$	Chlorobenzene	$C_6H_{11}NCO$	200	93.0	87–89 (0.5)				
4-$CH_3C_6H_4$	Chlorobenzene	C_6H_5NCO	500	85.3	103–110 (0.9)				
2,5-$(CH_3)_2C_6H_3$	Chlorobenzene	*n*-C_4H_9NCO	150	60.5	95–97 (0.5)	163–164[d]	$C_{10}H_{13}NO_4S$	C: 49.36 H: 5.38 H: 5.75	C: 49.42 H: 5.47 N: 5.88
4-FC_6H_4	Chlorobenzene	*n*-C_4H_9NCO[e]	300	73.0	94–95 (0.9)	112–114[f]	$C_8H_8FNO_4S$	N: 6.00	N: 5.75
4-ClC_6H_4	Chlorobenzene	*n*-C_4H_9NCO[g]	100	89.0	92–93 (0.4)[h]				
2,5-$(Cl)_2C_6H_3$	Chlorobenzene	*n*-C_4H_9NCO[g]	1000	32.0	118–120 (0.5)	188–189[i]	$C_8H_7Cl_2NO_4S$	C: 33.81 H: 2.48 N: 4.92	C: 33.95 H: 2.72 N: 5.12
3,4-$(Cl)_2C_6H_3$	Chlorobenzene	*n*-C_4H_9NCO[g]	300	91.3	128–130 (0.6)	142–143[i]	$C_8H_7Cl_2NO_4S$	C: 33.81 H: 2.48 N: 4.92	C: 33.93 H: 2.60 N: 5.28
4-BrC_6H_4	Chlorobenzene	*n*-C_4H_9NCO[g]	165	89.5	117–120 (1.2) (38–40)	121–122[f]	$C_8H_8BrNO_4S$	N: 4.76	N: 4.32
4-$CH_3OC_6H_4$	Chlorobenzene	*n*-C_4H_9NCO	200	87.8	130–133 (0.4)	126–127[f]	$C_9H_{11}NO_5S$	N: 5.72	N: 5.98
4-$O_2NC_6H_4$	*o*-Dichlorobenzene	*n*-C_4H_9NCO[g]	100	81.1	137–143 (0.4) (70–73)	152–155[f]	$C_8H_8N_2O_6S$	C: 36.92 H: 3.09 N: 10.76	C: 36.57 H: 3.27 N: 10.91
3-$O_2NC_6H_4$	*o*-Dichlorobenzene	*n*-C_4H_9NCO	175	78.0	152–153 (1.0) (84–86)	124–125[f]	$C_8H_8N_2O_6S$	C: 36.92 H: 3.09 N: 10.76	C: 36.92 H: 3.08 N: 10.53

[a] 20 mole % of catalyst generally has been used. [b] Lit.[2] bp 139° (13.5 mm). [c] Lit.[4] bp 90–93° (0.05 mm). [d] Recrystallized from aqueous ethanol. [e] 30 mole % catalyst. [f] Recrystallized from ethylene dichloride. [g] 40 mole % catalyst. [h] Lit.[5] bp 78–79° (0.005 mm). [i] Recrystallized from methanol.

arylsulfonyl-3-arylurea becomes the rate-determining step.

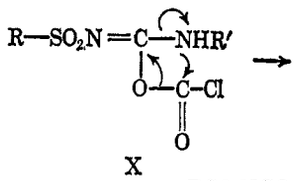
The arylsulfonyl isocyanates were colorless or light yellow (nitro derivatives) liquids or low-melting solids capable of distillation *in vacuo* without decomposition and were characterized by the following absorption in the infrared: ν_{as-NCO} at 4.46–4.9 μ, ν_{as-SO-} at 7.2–7.3 μ, and ν_{as-SO_2-} at 8.4–8.5 μ. Their color stability was found to be far superior to that of the aryl isocyanates, despite their high sensitivity to moisture. The addition of a strong base, such as potassium *t*-butoxide, caused no di- or trimerization, probably because the sulfonyl group enhances the resonance stabilization of the anion IX, and thereby lessens the probability for IX to attack a second molecule of arylsulfonyl isocyanate.

$$RSO_2NCO + R'O^{\ominus} \longrightarrow$$



IX

Two mechanisms can be visualized for the carbonyl chloride–arylsulfonylurea reaction: (1) formation of a pseudourea X which *via* a concerted reaction would afford the observed products; (2) formation of the allophanoyl chloride by direct N attack. The results obtained from the reaction of 1-*p*-tolylsulfonyl-3-*n*-butylurea with phosphorus pentachloride,[11] tend to strengthen the second possibility.



X

$$RSO_2NCO + R'NHCOCl \rightarrow R'NCO + HCl$$

The usefulness of these reactions with arylsulfonylureas lies in the facile paths they open to the synthesis of mono- and difunctional isocyanates. The conversion of primary amines or diamines to the corresponding isocyanates can be accomplished by preparing a sulfonylurea *in situ* from a sulfonyl isocyanate and the amine and reacting this urea with carbonyl chloride. To obtain an arylsulfonyl isocyanate, the corresponding sulfonamide can be reacted with an alkyl isocyanate to give the sulfonylurea which, on phosgenation, affords the desired isocyanate. Both routes regenerate the starting arylsulfonyl and alkyl isocyanate, respectively.

Experimental Section[12]

Reaction of 1-Arylsulfonyl-3-alkylureas with Carbonyl Chloride. General Procedure.—The specified amount of carbonyl

(11) H. Ulrich and A. A. R. Sayigh, *J. Org. Chem.*, **30**, 2779 (1965).

(12) Analyses were done by Schwarzkopf Microanalytical Laboratory, N. Y. The infrared spectra were obtained with the Perkin-Elmer Model 21 infrared spectrophotometer. The H^1 nmr spectra were obtained with a Varian A-60 instrument, and chemical shifts are in parts per million relative to TMS in carbon tetrachloride. The analyses by vapor phase chromatography were conducted on an F & M gas chromatograph, Model 720, which employed helium as a carrier gas and a 6-ft, silicon rubber column.

chloride (Table I) was added over a period of 150 min at 80–100° to 1 mole of the 1-arylsulfonyl-3-alkylurea dissolved in 1350 ml of chlorobenzene. The reaction mixture was heated to reflux and then purged with nitrogen. Fractional distillation (not higher than 200°) afforded the alkyl isocyanate and solvent, while distillation *in vacuo* of the residue afforded the arylsulfonyl isocyanate.

Reaction of Bis(*o*-tolylsulfonylcarbamoyl)alkylenediamines with Carbonyl Chloride. General Procedure.—The specified amount of carbonyl chloride (Table II) was added at the rate of 1 g/min at the given temperature interval to 0.06 mole of the bis(*p*-tolysulfonylcarbamoyl)alkylenediamine in 300 ml of *o*-dichlorobenzene (or chlorobenzene). The reaction could be followed in the infrared by the appearance of the isocyanato–NCO absorption at 4.4–4.5 μ and the disappearance of the urea–NH absorption at 2.97 μ. Fractional distillation *in vacuo* separated the solvent from the higher boiling alkylene diisocyanates and *p*-toluenesulfonyl isocyanate.

N,N′-Bis(*n*-butylcarbamoyl)toluene-2,4-disulfonamide (IV).—Sodium hydroxide (2 *N*, 50 ml) was added to 12.5 g (0.05 mole) of toluene-2,4-disulfonamide in 200 ml of acetone and the mixture heated to reflux. *n*-Butyl isocyanate (11 g, 0.11 mole) was added dropwise and the reaction mixture refluxed for an additional 3 hr. Evaporation of the acetone and acidification of the aqueous residue with dilute hydrochloric acid caused precipitation of a resinous material. This material was dissolved in glacial acetic acid, reprecipitated with the addition of water, and triturated with 2-propanol to afford 10.2 g (45.5%) of N,N′-bis(*n*-butylcarbamoyl)toluene-2,4-disulfonamide (IV): mp 175–178°; λ_{max}^{KBr} 3.05 (–NH), 3.3, 3.43, 6.02 (C=O), 6.5, 6.92, 7.47, 8.64, 9.18, and 11.18 μ.

Anal. Calcd for $C_{17}H_{28}N_4O_6S_2$: C, 45.63; H, 6.29; N, 12.49. Found: C, 45.78; H, 6.03; N, 12.39.

Toluene-2,4-disulfonyl Diisocyanate (V).—Carbonyl chloride (4.1 g, 0.041 mole) in 30 ml of chlorobenzene was added dropwise during 8 min with cooling and stirring to 8.96 g (0.02 mole) of N,N′-bis(*n*-butylcarbamoyl)toluene-2,4-disulfonamide (IV) in 60 ml of chlorobenzene. The reaction mixture was heated to reflux and carbonyl chloride then introduced at the rate of 1 g per min for 20 min. Purgation of the reaction mixture with nitrogen, followed by the removal of chlorobenzene and distillation *in vacuo* of the residue, afforded 2.3 g (38.3%) toluene-2,4-disulfonyl diisocyanate (V): bp 171–175° (1.8 mm); mp 48–53°; $\lambda_{max}^{CCl_4}$ 4.48 μ (–SO_2NCO). *n*-Butyl isocyanate (3.09 g, 76.6%) was contained in the chlorobenzene, as evidenced both by infrared absorption and by titration with di-*n*-butylamine.[13]

Refluxing a sample of the diisocyanate with excess methanol and then allowing the solution to cool afforded the crystalline bis(methylurethan), mp 80–83°.

Anal. Calcd for $C_9H_{14}N_2O_8S$: N, 8.17. Found: N, 7.90.

4-Isocyanatobenzenesulfonyl Isocyanate.—N-*p*-Sulfanilyl-N′-*n*-butylurea (27.1 g, 0.1 mole) was added gradually at 2° with stirring and ice cooling over a period of 6 min to 19.8 g (0.2 mole) of carbonyl chloride in 270 ml of chlorobenzene. After the reaction mixture had been stirring for 10 min, a slow stream of carbonyl chloride was introduced and the reaction temperature gradually raised to 130° (reflux). Refluxing the reaction mixture 90 min followed by purgation with nitrogen, filtration, and distillation afforded 6.8 g (68.7%) of *n*-butyl isocyanate[13] and 14.4 g (64.3%) of 4-isocyanatobenzenesulfonyl isocyanate: bp 115–120° (0.4 mm); mp 40–44°; $\lambda_{max}^{CHCl_3}$ 4.4 (–NCO), 4.48 (–SO_2NCO), and 7.25, 8.5 μ (SO_2).

Anal. Calcd for $C_8H_4N_2O_4S$: C, 42.85; H, 1.79; N, 12.49; S, 14.30. Found: C, 43.09; H, 2.17; N, 12.53; S, 14.28.

Addition of excess methanol to a sample of the diisocyanate afforded, after evaporation of some methanol, the crystalline bis(methylurethan), mp 208–210°.

Anal. Calcd for $C_{10}H_{12}N_2O_6S$: C, 41.65; N, 4.19; N, 9.71. Found: C, 41.59; H, 4.29; N, 9.34.

3-Isocyanatobenzenesulfonyl Isocyanate.—N-*m*-sulfanilyl-N′-*n*-butylurea (40 g, 0.15 mole) was added gradually at 2–5° with stirring and ice cooling over a period of 7 min to 30 g (0.3 mole) of carbonyl chloride in 400 ml chlorobenzene. After the reaction mixture had been stirring for 10 min, a slow stream of carbonyl chloride was introduced and the reaction temperature raised to 130° (reflux). Refluxing the reaction mixture for 60 min followed by purgation with nitrogen, filtration, and distillation afforded 10.1 g (68.1%) of *n*-butyl isocyanate[13] and 15.3 g (45.7%) of 3-isocyanatobenzenesulfonyl isocyanate: bp 135–136° (1.1 mm); $\lambda_{max}^{CHCl_3}$ 4.4 (NCO), 4.48 (SO_2NCO), and 7.28, 8.42 μ (SO_2).

Addition of excess methanol to a sample of the diisocyanate afforded, after evaporation of some methanol, the crystalline bis(methylurethan), mp 185–186°.

Anal. Calcd for $C_{10}H_{12}N_2O_6S$: C, 41.65; H, 4.19, N, 9.71. Found: C, 41.50, H, 4.04; N, 9.89.

2,5-Dimethoxy-N-*p*-sulfanilyl-N′-*n*-butylurea.—2,5-Dimethoxy-*p*-sulfanilamide (46.4 g, 0.2 mole) and 90 ml of acetone, followed by 19.8 g (0.2 mole) of *n*-butyl isocyanate, were added to 8 g (0.2 mole) of sodium hydroxide in 120 ml of water. An exothermic reaction ensued, the temperature rising to 50°. Filtration of the reaction mixture, evaporation of the acetone and acidification of the aqueous residue with dilute hydrochloric acid gave 30.3 g (45.8%) of 2,5-dimethoxy-N-*p*-sulfanilyl-N′-*n*-butylurea, mp 195–197° (methanol).

Anal. Calcd for $C_{13}H_{21}N_3O_5S$: C, 47.11; H, 6.38; N, 12.67. Found: C, 47.28; H, 6.52; N, 12.57.

4-Isocyanato-2,5-dimethoxybenzenesulfonyl Isocyanate (VII).—2,5-Dimethoxy-N-*p*-sulfanilyl-N′-*n*-butylurea (16.55 g, 0.05 mole) was added with cooling and stirring to 15 g (0.15 mole) of carbonyl chloride in 170 ml of chlorobenzene. Carbonyl chloride was introduced at the rate of 1 g/min and the reaction temperature concomitantly raised to 130° (reflux). Purgation of the reaction mixture with nitrogen for 25 min, followed by removal of the solvent and distillation *in vacuo* of the residue, afforded 4.4 g (31%) of 4-isocyanato-2,5-dimethoxybenzenesulfonyl isocyanate (VII), bp 160–181° (0.09–1.00 mm). On standing the material solidified and was crystallized repeatedly from carbon tetrachloride to give 4-isocyanato-2,5-dimethoxybenzenesulfonamide (VIII), mp 195–196°.

Anal. Calcd for $C_9H_{10}N_2O_5S$: N, 10.84. Found: N, 11.08.

Refluxing a sample of the 4-isocyanato-2,5-dimethoxybenzenesulfonyl isocyanate with excess methanol and then allowing the solution to cool afforded the crystalline bis(methylurethan), mp 229–231°.

Anal. Calcd for $C_{12}H_{16}N_2O_8S$: C, 41.37; H, 4.62; N, 8.04. Found: C, 41.30; H, 4.62; N, 8.24.

Reaction of N-(4-Chloro-*o*-sulfanilyl)-N′-*n*-butylurea with Carbonyl Chloride.—N-(4-Chloro-*o*-sulfanilyl)-N′-*n*-butylurea (45.8 g, 0.15 mole) was added with cooling and stirring to 50 g (0.5 mole) of carbonyl chloride in 450 ml of chlorobenzene. Carbonyl chloride was introduced at the rate of 1 g/min and the reaction temperature concomitantly raised to 130° (reflux). After purgation of the reaction mixture with nitrogen for 30 min, there was obtained 30.5 g (87.6%) of 6-chloro-2 H-1,2,4-benzothiadiazin-3-(4H)-one 1,1-dioxide (VI),[14] mp 316–317°. *n*-Butyl isocyanate (11.55 g, 78.04%) was contained in the residual chlorobenzene, as evidenced both by infrared absorption and by titration with di-*n*-butylamine.[13]

Direct Phosgenation of Arylsulfonamides. General Procedure.—The arylsulfonamide (0.5 mole) was dissolved or suspended in chlorobenzene (10% solution) and the mixture distilled azeotropically to remove traces of water. The mixture was cooled to 100° and 0.1 mole of *n*-butyl isocyanate added. The resultant solution was heated to reflux and the specified quantity of carbonyl chloride (Table III) added at the rate of 1 g/min. A vigorous evolution of hydrogen chloride accompanied the reaction. Purgation with nitrogen at 130–132° for 30 min, followed by distillation of the *n*-butyl isocyanate with the solvent and distillation *in vacuo* of the residue afforded the arylsulfonyl isocyanates in high purity.

Methylarylsulfonylcarbamates. General Procedure.—A 0.01-mole sample of the arylsulfonyl isocyanate was added dropwise to 20 ml of methanol The reaction was exothermic. Evaporation of the solvent afforded the methyl arylsulfonylcarbamate in quantitative yield and of high purity.

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(13) Determined by titration with di-*n*-butylamine according to the procedure of S. Siggia and J. G. Hanna, *Anal. Chem.*, **20**, 1084 (1948).

(14) L. Raffa, M. DiBella, and A. Monzani, *Farmaco (Pavia) Ed. Sci.*, **15**, 716 (1960).