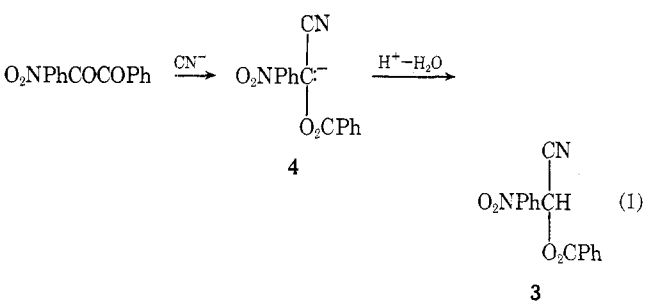
several solvent combinations, as a model for "active aldehyde" intermediates in (a) the benzoin condensation and (b) thiamine action in biological systems. This research group[3,4] demonstrated that **1**, generated in the presence of a variety of added electrophiles, gave rise to a spectrum of products.

While in all instances[1-4] the products obtained from the benzil–cyanide reaction has been logically accounted for by invoking the intermediacy of **1**, the intermediate, *per se*, has not been isolated. In any mechanistic study, the trapping or otherwise isolation of a proposed intermediate is considered of value in the compilation of data which allows for eventual elucidation of the reaction path. As an extension of our earlier work,[2] this report notes the isolation of the nitro derivative of intermediate **1**, 4-nitromandelonitrile benzoate (**3**), in good yield from the reaction of 4-nitrobenzil with cyanide in DMSO or *N,N*-dimethylformamide (DMF). The reaction is shown in eq 1. In no experiment was the corresponding stilbenediol dibenzoate detected. Thus, the role of cyanide ion is now one of reactant in contrast to that of catalyst in the reaction with benzil.



These results are of added interest in view of the findings of Kwart and Baevsky[1] that 4-nitrobenzil and cyanide ion are unreactive in alcoholic solution. These investigators observed the formation of a stable, colored solution which readily reverted to starting material. The generation of a stable semiquinone was considered a possibility. It seems reasonable, in view of our findings, that an alternate explanation can be offered. Thus, the reaction might have failed owing to the relatively low ratio (implied, though not stated[1]) of cyanide catalyst to 4-nitrobenzil. Perhaps cyanide was simply consumed to form trace amounts of **4**.

The success of the reaction in aprotic solvents presumably results from the inertness of **4** toward another molecule of 4-nitrobenzil. The negative charge is more completely delocalized in **4** (relative to **1**) owing to the favorable location of the nitro substituent.

The obvious analogy is drawn between the benzil–cyanide reaction and the benzoin condensation where cyanide also acts both as the nucleophile and as a group which delocalizes the negative charge on the intermediate carbanion.[5] The analogy is extended in that, while 4-nitrobenzaldehyde readily undergoes cyanohydrin formation,[6] it fails in the benzoin condensation.[7] As in our reaction, the best explanation seems to be that the delocalizing influence of the nitro group renders the intermediate so inert as to react no further with starting material.

Identification of **3** was accomplished by spectral analysis and comparison with a sample of benzoylated 4-nitromandelonitrile. It is interesting that C≡N absorption, in the 2100–2400-cm^{-1} region of the ir spectrum, is absent. However, this observation is in agreement with an earlier report that the C≡N stretch in compounds where the cyano group is attached to oxygenated carbon is "quenched" to the point of being extremely weak or not observable at all.[8]

Experimental Section[9]

Starting Materials. 4-Nitrobenzil was prepared according to the method of Womack, Campbell, and Dodd.[10] The solvents, DMSO and DMF, were distilled from calcium hydride at reduced pressure. Other materials were available in reagent grade and were used without further purification.

4-Nitrobenzil and Sodium Cyanide in DMSO. Sodium cyanide (0.25 g, 5.1 mmol) was stirred into 40 ml of solvent under an atmosphere of nitrogen. 4-Nitrobenzil (1.28 g, 5.0 mmol) was added in a single portion at room temperature. The solution at once turned deep violet in color. After 1.5 min, the reaction mixture was poured into an acidified ice–water slurry. The resulting suspension was extracted with ether. The ether layer was washed with water, dried over sodium sulfate, and evaporated. The residue (red-brown oil) was triturated with ethanol to afford light yellow crystals (0.82 g, 58%) of 4-nitromandelonitrile benzoate (**3**), mp 112–114° (ethanol).

Anal. Calcd for $C_{15}H_{10}N_2O_4$: C, 63.83; H, 3.54; N, 9.93. Found: C, 63.80; H, 3.69; N, 10.07.

The nmr spectrum showed a 1 H singlet (methinyl) at δ 6.9 and a 9 H multiplet at δ 7.5–8.5 (aromatic). The ir spectrum showed carbonyl absorption at 1725 cm^{-1}. No absorption for C≡N was observed.[8] The mass spectrum (30 eV) showed *m/e* (rel intensity) 282 (M^+), 255 (8), 106 (46), 77 (100), m* 230.6.

4-Nitromandelonitrile Benzoate (3). The procedure used by Cronyn[11] for the preparation of 3-nitromandelonitrile benzoate was adopted. A suspension was prepared in an ice bath from 4-nitrobenzaldehyde (3.77 g, 25 mmol) and 5 ml of water, to which was added benzoyl chloride (3.64 g, 25.8 mmol). Potassium cyanide (2.0 g, 31.5 mmol) in 3 ml of water was added in one portion with stirring. The resulting yellow crystals were filtered and triturated with ethanol to afford the crude product (5.0 g, 70.8%, mp 108–111°). Recrystallization from ethanol resulted in an almost colorless sample, mp 114–115°. The material was identical with **3** in the previous experiment as shown by mixture melting point and comparison of spectral data.

Acknowledgment. We are grateful to J. Michael Robinson, Paul Moser, and Paula Watts at Louisiana State University for assistance in obtaining some of the spectral data.

Registry No.—**3**, 51130-02-0; 4-nitrobenzil, 22711-24-6; NaCN, 143-33-9.

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Synthesis of Alkanesulfonyl Isocyanates by Thermolysis of Trimethylsilylated Sulfonyl Carbamates

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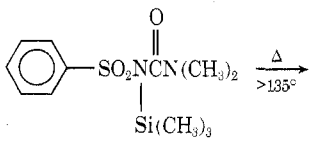
Received October 24, 1973

A communication by Greber and Krideldorf[1] describing the thermolysis of N-silylated carbamoyl chlorides, anhy-

drides, or urethanes to yield isocyanates stimulated our investigation of a new approach to sulfonyl isocyanate synthesis. We have found that both aryl- and alkylsulfonyl carbamates can be silylated easily and subsequent thermolysis of the trimethylsilyl intermediates produces the corresponding sulfonyl isocyanates in excellent yields. The new procedure eliminates a hazardous phosgenation step normally required in sulfonyl isocyanate synthesis[2,3] and minimizes the formation of difficultly separable by-products. The sulfonyl isocyanates are not contaminated by the sulfonyl chlorides which are normally present in isocyanates produced by a high-temperature phosgenation process. Furthermore, alkanesulfonyl isocyanates cannot be prepared by direct phosgenation and alternate procedures[4,5] are very inefficient. This paper describes a simple procedure for preparing pure aryl- or alkanesulfonyl isocyanates from readily available reagents.

Either sulfonyl carbamates or sulfonylureas can be silylated by treatment with trimethylchlorosilane in the presence of tertiary amines. Sulfonylureas are easier to synthesize but their silylated derivatives decompose to isocyanates and silylated sulfonamides rather than the desired products. In fact, Itoh, *et al.*,[6] has shown that pyrolysis of *N*-benzenesulfonyl-*N*-trimethylsilyl-*N'*,*N'*-dimethylurea (1) produces methyl isocyanate and *N*-trimethylsilyl-*N*-methylsulfonamide (2). Apparently silylated sulfonylureas do not undergo direct thermolysis; so these derivatives cannot be utilized as starting materials for a sulfonyl isocyanate synthesis.



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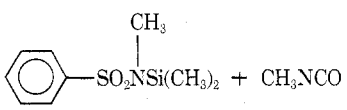


2

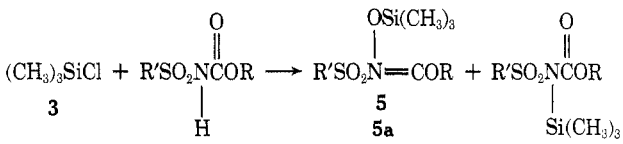
Silylated Sulfonyl Carbamates. *O*-Alkylsulfonyl carbamates can be synthesized by treatment of the appropriate sulfonamide with an alkyl chloroformate in the presence of potassium carbonate.[7] Alkyl chloroformates must be used in this step because aryl chloroformates participate in a multistep, base-catalyzed condensation to yield 1,3-bis(alkyl- or -arylsulfonyl)ureas instead of the desired *O*-aryl-*N*-alkyl- or -arylsulfonyl carbamates.[8] Silylation of *O*-alkyl-*N*-arylsulfonyl carbamates occurs readily when a hydrocarbon solution of the derivatives is treated with trimethylchlorosilane (3) in the presence of triethylamine. Triethylammonium hydrochloride precipitates quantitatively from the reaction medium when a solution of triethylamine is added to the reagents; subsequent isolation of the silylated intermediate simply involves removal of the amine salt by filtration followed by evaporation of the solvent under reduced pressure.

The progress of the silylation can be followed spectrophotometrically. Disappearance of the NH (3200 cm^{-1}) and a reduction in intensity of carbonyl (1760 cm^{-1}) infrared absorption bands is accompanied by the appearance of new bands at 1600 (C=N) and 1085 cm^{-1} (SiO). A linear correlation between this SiO absorption band intensity and the extent of reaction as estimated by nmr existed throughout a conversion range of 0–90%. The decrease in the carbonyl absorption intensity is indicative of extensive O-silylation; this is confirmed by the relative intensities of the silylmethyl absorptions in the nmr spectrum. The ratio of O-silylated to N-silylated derivatives is dependent upon the nature of R'. For example, *O*-neopentyl-*N*-*p*-toluenesulfonyl carbamate (4) yields a product mixture composed primarily of the O-silylated (5) derivative. In contrast, *O*-ethyl-*N*-methylsulfonyl carbamate (4a) exhibits a strong carbonyl absorption (1740 cm^{-1}) which is consistent with a mixture containing predominantly N-silylated product (6a). Both N- and O-silylated products undergo thermal decomposition to yield the corresponding sulfonyl isocyanates. This suggests that a rapid equilibration between the two isomers is occurring under the thermolysis conditions.

Table I
Thermolysis of Silylated *O*-Neopentyl-*N*-*p*-toluenesulfonyl Carbamate[a]

Run	Temp, °C	Silylated 5 concn, mol/l.	k_1, sec^{-1} [b] × 10^4	$t_{1/2}$, min
1	110	0.191	3.39	34.1
2	110	0.057	3.71	31.1
3	110	0.096	3.74	30.9
4	110	0.120	3.12	37.0
Plot of initial rates of runs 1–4			3.50	33.0
5	80	0.120	0.52	222.1
6	90	0.120	1.08	107.0
7	120	0.120	8.14	14.2

[a] Rates measured by time dependence of absorption at 2235.5 cm^{-1} (ν_{NCO}) in xylene. [b] First-order rate constants; correlation coefficient >0.99.



4, R = neopentyl; R' = tolyl
4a, R = ethyl; R' = methyl

Thermal Dissociation. Thermolysis of trimethylsilylated carbamates can be effected by heating the derivatives in inert solvents such as xylene, chlorobenzene, or acetonitrile. The dissociation appears to be favored by polar solvents, since replacement of the hydrocarbon solvent used in the silylation procedure with acetonitrile before completing the thermolysis reduces the temperature required to liberate the sulfonyl isocyanate. Silylated *O*-phenyl-*N*-*p*-toluenesulfonyl carbamate decomposes slowly at 25°; the corresponding *O*-neopentyl derivative must be heated to 60° before a noticeable thermolysis occurs.

The thermolysis rate of a mixture of 5 and 6 was determined by observing the development of the isocyanate absorption band at 2235.5 cm^{-1}. The reaction exhibited first-order kinetics to at least 90% conversion. Furthermore, a plot of the initial rates exhibited by different concentrations of substrate was linear and yielded a rate constant comparable to those calculated for an irreversible first-order process. (Table I). An Arrhenius plot of the data is linear and indicates an activation energy of 19.4 ± 0.6 kcal/mol. The activation entropy is −24.6 ± 0.6 eu, which suggests an oriented cyclic transition state as exemplified by structures 7 or 8 in Scheme I.

We have shown that the cleavage occurs at the acyl carbon by the reaction sequence outlined in Scheme II. Optically active (*R*)-(−)-2-octanol (9) was allowed to react with *p*-toluenesulfonyl isocyanate to produce 10. Silylation of 10 followed by thermolysis (path B) enabled us to isolate optically active alkoxysilane 11, $[\alpha]^{25}D$ − 13.58°. The thermolysis proceeds with complete retention of configuration of the alkoxy substituent. The reaction sequence also suggests a new technique for resolving alcohols, since the sulfonyl carbamate intermediate would

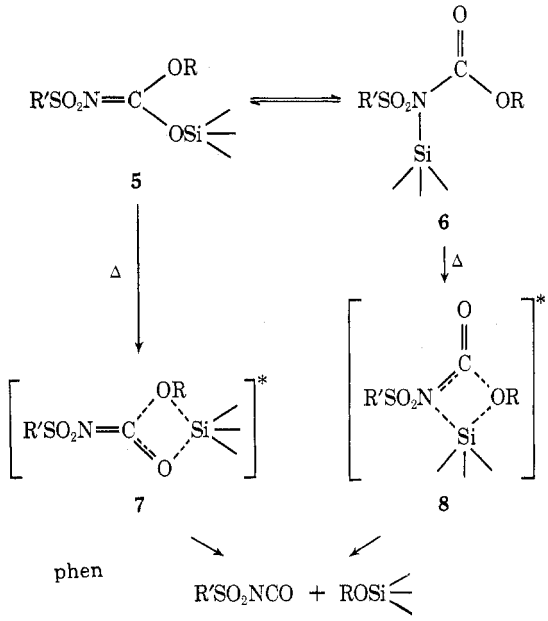
Table II
Preparation of Alkylsulfonyl Isocyanates by Thermolysis Procedure

$$RSO_2NH_2 \xrightarrow[K_2CO_3]{CH_3CH_2OCCl} RSO_2NHCOEt \xrightarrow[2.\ \Delta]{1.\ \text{silylation}} RSO_2NCO \xrightarrow{R'OH} RSO_2NHCOR'$$

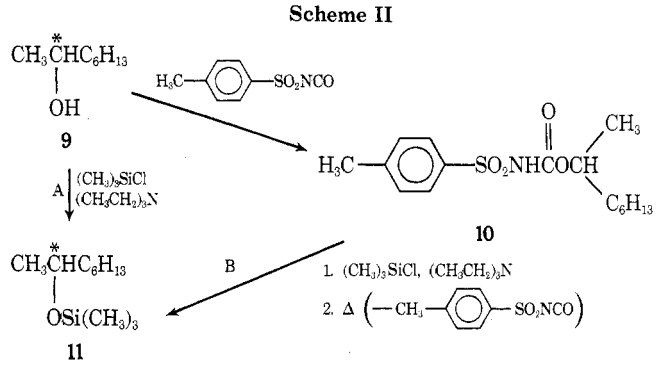
Expt	R	Sulfonyl carbamate[a] Registry no.	Yield, %	Mp, °C	Registry no.	Sulfonyl isocyanate Yield, %	Bp, °C (mm)	ν_{NCO}, cm^{-1}	Registry no.	Carbamate derivative[a] R′	Mp, °C	Registry no.
12	CH_3	3144-09-0	70.3	55 57	49671-33-2	67–79	49 (2)	2275	3611-92-5	$(CH_3)_3CCH_2$	79	51003-68-0
13	CH_3CH_2	1520-70-3	65.5	70–71	51003-65-7	45–62	76 (10)	2260	14604-85-4	Ph	125–127	51003-69-1
14	$CH_3CH_2CH_2CH_2$	3144-04-5	70	Oil	51003-66-8	72	78 (2)	2265	3670-24-4	Ph	68–69	51003-70-4
15	$PhCH_2$	4563-33-1	72	101–102	46731-59-3	62	96 (0.5)	2260	51003-67-9	$(CH_3)_3CCH_2$	109–110	51003-71-5

[a] Satisfactory analytical data were reported for all new compounds listed in the table.

Scheme I



Scheme II



probably form a diastereomeric salt mixture with an optically active amine.

Synthetic Applications. Since most arylsulfonyl isocyanates can be prepared by direct phosgenation,[3] the primary application of the thermolysis procedure is alkanesulfonyl isocyanate preparation. We have applied this procedure to the synthesis of methane- (12), ethane- (13), *n*-butane- (14), and α-toluenesulfonyl isocyanate (15) and the results are summarized in Table II. No attempt was made to isolate the silyl derivatives; the crude silylation mixture was pyrolyzed and the alkanesulfonyl isocyanate was isolated by fractional distillation. The sulfonyl isocyanates are extremely reactive liquids which are difficult to characterize; however, they react quantitatively with either neopentyl alcohol or phenol to produce stable crystalline alkanesulfonyl carbamate derivatives. The range of yields cited in Table II represents the difference between actually isolating the alkanesulfonyl isocyanate by distillation (lower values) and isolating the sulfonyl carbamate derivative which was prepared directly by adding the alcohol to the thermolysis reaction mixture.

In contrast to the reduced reactivity of alkyl isocyanates relative to aryl isocyanates, the alkanesulfonyl isocyanates appear to be comparable to benzenesulfonyl isocyanates in their reactivity toward alcohols and phenols. For example, treatment of wood cellulose with butanesulfonyl isocyanate produced an acetone-soluble alkanesulfonyl carbamylated cellulose in 30 min. Similar results were obtained using the thermolysis product mixture in place of the pure isocyanate. The properties of the cellulose derivative were analogous to those reported for *p*-toluenesulfonyl carbamylated cellulose.[9]

Experimental Section[10]

Reagents. Trimethylchlorosilane (3) was purified by distillation from 5 wt % sucrose and tri-*n*-butylamine to remove polychlorosilane derivatives.[11] The alkyl sulfonamides were prepared from the corresponding sulfonyl chlorides using a benzene solution of anhydrous ammonia.[12] Commercially available *p*-toluenesulfonyl isocyanate was used without further purification for preparative procedures. Since this material is contaminated with *p*-toluenesulfonyl chloride, which is difficult to remove, pure *p*-toluenesulfonyl isocyanate, bp 100° (0.5 mm), was prepared *via* the silylated carbamate procedure to use for infrared kinetic studies. *O*-Ethyl-*N*-alkylsulfonyl carbamates were prepared according to the general procedure of Cassady, *et al.*;[7] yields and melting points are reported in Table II. *O*-Alkyl-*p*-toluenesulfonyl carbamates were obtained by addition of the appropriate alcohol to a solution of *p*-toluenesulfonyl isocyanate in ether.

Silylation of *O*-Neopentyl-*N*-*p*-toluenesulfonyl Carbamate (4). The following general procedure was used to prepare the silylated sulfonyl carbamates. A solution of 3.84 g (13.46 mmol) of 4 in a mixture of 5 ml of acetonitrile and 30 ml of benzene was mixed with 5.85 g (54 mmol) of 3 and cooled in an ice bath. After slowly adding a solution of 1.37 g (13.5 mmol) of triethylamine in 10 ml of benzene, the reaction mixture was stirred at 20° for 1.5 hr. The excess trimethylchlorosilane was evaporated *in vacuo*, 25 ml of cyclohexane was added, and the triethylammonium salt was removed by filtration. The filtrate was concentrated *in vacuo* to yield 4.84 g of a mixture of 5 and 6: nmr (benzene-d_6) δ 7.88 (d, 2 H), 6.87 (d, 2 H), 3.70 (s, 2 H), 2.09 (s, 3 H), 0.81 (s, 9 H), 0.23 (s, 6.8 H), 0.18 (s, 1.2 H). Although the absorptions below δ 0.5 were slightly broader than expected, it was not possible to resolve these signals and confirm the presence of an isomer mixture. The spectrum is consistent with a 90% yield of an 85:15 mixture of 5 and 6, based upon the relative intensities of the silylmethyl proton absorption.

Silylation of *O*-ethyl-*N*-methylsulfonyl carbamate was conducted exactly as described above using 3.35 g (20 mmol) of **4a**, 8.7 g (80 mmol) of $(CH_3)_3SiCl$, and 2.02 g (20 mmol) of trimethylamine. Evaporation of the solvent mixture yielded 4.63 g of viscous oil, nmr (benzene-d_6) δ 3.99 (q, 2 H), 2.95 (s, 3 H), 1.09 (t, 3 H), 0.37 (s, 2.1 H), 0.28 (s, 4.9 H).

***O*-Ethyl-*N*-ethylsulfonyl carbamate (4b)** was silylated using 3.63 g (20 mmol) of **4b**, 8.7 g (80 mmol) of $(CH_3)_3SiCl$, and 2.02 g (20 mmol) of triethylamine; 4.71 g of oil remained, nmr (benzene-d_6) δ 3.98 (a, 2 H), 3.05 (m, 2.8 H) 1.17 (d of t, 7.7 H) 0.41, (s, 2.1 H), 0.28 (s, 4.4 H). The residual oil appears to be a mixture of **5b** and **6b**; ir (neat) 2250 (NCO), 1740 (C=O), and 1085 cm^{-1} (SiO) confirms this analysis.

Butanesulfonyl isocyanate (14) was prepared directly from *O*-ethyl-*N*-butanesulfonyl carbamate (**16**) without isolating the silylated intermediate. Addition of triethylamine (21.2 g, 0.209 mol) to a cooled solution of 43.7 g (0.209 mol) of **16** and 68.5 g (0.63 mol) of **3** in 140 ml of benzene effected the silylation. After the reaction mixture was stirred for 2 hr, the excess trimethylchlorosilane and ~25 ml of solvent were evaporated under reduced pressure. The residue was filtered under nitrogen and then the remaining solvent was evaporated. The residual oil was redissolved in 70 ml of acetonitrile and refluxed for 2 hr. Evaporation of the acetonitrile followed by vacuum distillation of the residue yielded 24.5 g (72%) of **14**: bp 78° (3 mm); ir (neat) 2240, 1350, 1150 cm^{-1}; nmr (CD_3CN) δ 3.2 (t, 2 H), 1.76–0.86 (m, 4 H), 0.67 (t, 3 H).

A similar procedure was utilized to prepare each of the sulfonyl isocyanates cited in Table II.

(−)-2-Octyloxytrimethylsilane (11). Method A. A solution of 5.38 g (0.041 mol) of **9**, $[\alpha]^{25}D$ (cyclohexane) −8.57°, in 50 ml of benzene was treated with 13.3 g (0.122 mol) of **3** and cooled to 5°. Following injection of 4.12 g (0.041 mol) of triethylamine, the mixture was allowed to warm to 37° and stirred for 3 hr. The excess trimethylchlorosilane was evaporated under reduced pressure, the triethylammonium chloride was removed by filtration under nitrogen, and the filtrate was treated with 2.0 g of *p*-toluenesulfonyl isocyanate to remove unreacted alcohol. Fractional distillation of the filtrate yielded 6.12 g (74%) of **11**, bp 70° (10 mm), $[\alpha]^{25}D$ (cyclohexane) −13.58°.

Method B. A solution of 9.70 g (0.049 mol) of *p*-toluenesulfonyl isocyanate in 40 ml of ether was mixed with an ethereal solution of **9** (6.40 g in 10 ml). After 1 hr the ether was evaporated and the residual oil **10**) was used without further purification. The silylation of **10**, 14.9 g (0.045 mol), with 14.7 g (0.135 mol) of **3** was catalyzed by addition of 4.6 g of triethylamine to a benzene solution of the reagents. The silylated sulfonyl carbamate was isolated and thermolyzed in acetonitrile in the usual manner. Fractional distillation of the product mixture yielded 8.12 g (74.5%) of **11**, bp 63° (6 mm), $[\alpha]^{25}D$ (cyclohexane) −14.68°.

Anal. Calcd for $C_{11}H_{25}OSi$: C, 65.62; H, 12.41; Si, 13.92. Found: C, 65.32; H, 12.38; Si, 13.67.

Reaction of *n*-Butylsulfonyl Isocyanate with Cellulose. A stirred, nitrogen-flushed mixture of 1.00 g (0.006 molar equiv) of wood cellulose in 50 ml of anhydrous pyridine was treated with 4.00 g (0.027 mol) of *n*-butylsulfonyl isocyanate at 85° for 6 hr. A clear solution was obtained within 30 min. The product was precipitated by pouring the reaction mixture into 500 ml of cold 50% ethanol–water which had been acidified with 50 ml of concentrated HCl. The polymer was dissolved in acetone, reprecipitated with acidified ice water, washed free of excess acid, and dried *in vacuo* at 60° for 12 hr; 3.63 g (D.S. = 2.6) of white powder was obtained. The butylsulfonyl carbamylated cellulose was soluble in acetone, DMF, and 2% NaOH, and swollen by ethanol.

Registry No.—**3**, 75-77-4; **4**, 32363-28-3; **5**, 51003-72-6; **5b**, 51003-73-7; **6**, 51003-74-8; **6a**, 51003-75-9; **6b**, 51003-76-0; **9**, 51003-19-1; **11**, 51003-20-4; *p*-toluenesulfonyl isocyanate, 4083-64-1; $CH_3CH_2O_2CCl$, 541-41-3.

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Lewis Acid Catalyzed Addition of Isocyanates to Sulfonamides

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Received October 24, 1973

The potential chemotherapeutic value of arylsulfonylureas as oral hypoglycemic agents has promoted intensive interest in their synthesis and chemical properties. Most of the preparative procedures described in the literature utilize arylsulfonamide salts, generated by inorganic bases or tertiary amines, as nucleophiles to add to isocyanates and related derivatives,[1] or to *sym*-1,3-dialkylureas.[2] Recently, an improved method for the preparation of arylsulfonyl isocyanates has increased the applicability of these highly reactive intermediates in arylsulfonylurea preparations.[3] We wish to describe a new approach to arylsulfonylurea synthesis which involves the direct condensation of arylsulfonamides with alkyl or aryl isocyanates in the presence of Lewis acid catalysts.

The Friedel–Crafts condensation of isocyanates with aromatic compounds in the presence of aluminum chloride was first reported by Leuckart in 1885.[4] This reaction has been evaluated more recently by Effenberger and Gleiter and the electrophilic character of the condensation was established.[5] The Friedel–Crafts reactivity of an isocyanate–Lewis acid complex toward the aromatic nucleus is