Desulfurization of 5.—By the same procedure described for desulfurization of **4**, 3.0 g of **5** was desulfurated to yield 1.3 g (48%) of 3,3′-diethylbiphenyl (**6**): bp 135–137° (1.3 mm); n^{20}D 1.5762; uv max (95% EtOH) 251 mμ (ε 16,745). The ir and nmr were identical in all respects to the ir and nmr of **6** obtained in the desulfurization of **4**.

2,6-Diacetyldibenzothiophene 5,5-Dioxide (7).—A mixture of 3.0 g of **3**, 10 ml of 30% H_2O_2, and 50 ml of HOAc was refluxed for 1 hr and cooled to room temperature, and the product was filtered. Recrystallization from acetonitrile gave 3.1 g (92%) of **7**: mp 303° dec; uv max (DMF) 333 mμ (ε 844); ir (KBr) 1695, 1681 (C=O), 1310, 1162 cm^{-1} (sulfone); nmr (CF_3COOH/$CDCl_3$) δ 2.83 (s, 3, CH_3), 2.87 (s, 3, CH_3).

Anal. Calcd for $C_{16}H_{12}O_4S$: C, 63.99; H, 4.03; S, 10.67. Found: C, 64.19; H, 3.95; S, 10.72.

2,8-Diacetyldibenzothiophene 5,5-Dioxide (8).—By the same procedure used in the oxidation of **3**, 6.0 g of **2** was oxidized, yielding 5.7 g (84%) of **8** after crystallization from acetonitrile: mp 272–277°; uv max (DMF) 377 mμ (ε 1430); ir (KBr) 1690 (C=O), 1312, 1169 cm^{-1} (sulfone); nmr (CF_3CO_2H/$CDCl_3$) δ 2.87 (s, 6, CH_3).

Anal. Calcd for $C_{16}H_{12}O_4S$: C, 63.99; H, 4.03; S, 10.67. Found: C, 64.24; H, 4.05; S, 10.64.

Registry No.—**1**, 132-65-0; **2**, 35105-75-0; **3**, 35105-76-1; **4**, 35105-77-2; **5**, 35105-78-3; **6**, 13049-38-2; **7**, 35105-80-7; **8**, 35105-81-8.

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Synthesis of 1-(*p*-Iodobenzenesulfonyl)-3,5-di-*n*-propyl Isocyanurate

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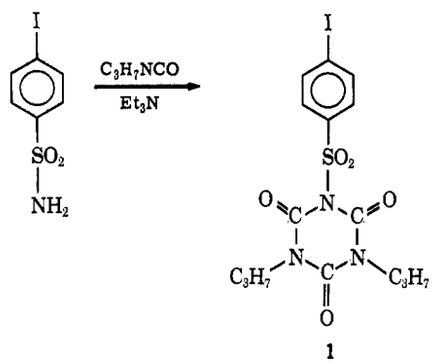
The base-catalyzed reaction of arylsulfonamides with alkyl isocyanates is a valuable synthetic method for the preparation of arylsulfonylureas. During studies aimed at the synthesis of 1-(*p*-iodobenzenesulfonyl)-3-*n*-propylurea-^{125}I, we found that a base-insoluble product was formed when the reaction was carried out with an excess of *n*-propyl isocyanate.[1] This base-insoluble product was identified as 1-(*p*-iodobenzenesulfonyl)-3,5-di-*n*-propyl isocyanurate (**1**).

Tri-N-substituted, di-N-substituted, and mono-N-substituted isocyanurates have been synthesized[2–4] and studied, but no 1-arylsulfonyl-3,5-dialkyl isocyanurates have been reported. The formation of **1**, therefore, represents not only a novel reaction but also a new chemical entity. The reaction most likely involves the base-catalyzed condensation of *p*-iodobenzenesulfonamide with a threefold excess of *n*-propyl isocyanate with the subsequent elimination of *n*-propylamine. The transient existence of a series of anionic intermediates can be justified on the basis of a delocalization of the developing negative charge as proposed by Ulrich[5] for analogous reactions.



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No mass ion occurred in the high-resolution mass spectrum of this compound under normal conditions; however, a small peak did occur at *m/e* 479 when the instrument was overloaded with sample. The prominent high mass ion in the mass spectrum occurred at *m/e* 415. This differs by sulfur dioxide from the proposed structure. The loss of sulfur dioxide upon electron impact has previously been reported in sulfonylureas[6] and in *O*-alkyl-*N*-arylsulfonyl carbamates.[7] The prominent ions in the mass spectrum of **1** (Table I)

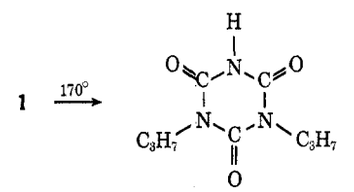
TABLE I

PROMINENT IONS IN THE MASS SPECTRUM OF 1-(*p*-IODOBENZENESULFONYL)-3,5-DI-*n*-PROPYL ISOCYANURATE

m/e	Ion	Per cent total ionization
415	$C_{15}H_{18}IN_3O_3^+$	12.50
374	$C_{12}H_{13}IN_3O_3^+$	8.75
332	$C_9H_7IN_3O_3^+$	2.70
288	$C_8H_5IN_2O_2^+$	13.25
267	$C_6H_4IO_2S^+$	22.50
245	$C_7H_4INO^+$	26.25
203	$C_6H_4I^+$	50.50
56	$C_2H_2NO^+$	51.25
43	$C_3H_7^+$	61.25

can be accounted for by fragmentation of the molecule in a manner analogous to that reported for tolbutamide[6] and for ethyl *N*-methyl-*N*-(*p*-toluenesulfonyl)carbamate.[7]

Heating **1** at 170° in DMF–H_2O afforded 1,3-di-*n*-propyl isocyanurate (**2**), thus providing chemical evidence in support of the proposed structure of **1**.



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Experimental Section

Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. Melting points were taken on a Fisher-Johns melting point apparatus and are corrected. Ir spectra were taken on a Perkin-Elmer 337 spectrophotometer. Nmr spectra were obtained with a Varian A-60 spectrometer in $CDCl_3$ at a concentration of 10% with TMS as an internal reference. Mass spectra were obtained on an Associated Electrical Industries MS902 Double Focusing High Resolution Mass Spectrometer equipped with a Honeywell 7600 Frequency Modulated Analog Tape Reader. The spectra were run at 70 eV. Chromatogram strips (K301R) were used for tlc, and the spots were detected with uv light.

1-(*p*-Iodobenzenesulfonyl)-3,5-di-*n*-propyl Isocyanurate (1).—A solution of 0.5 g (0.0018 mol) of *p*-iodobenzenesulfonamide in 5 ml (0.052 mol) of *n*-propyl isocyanate and 0.1 ml of triethylamine was refluxed with stirring for 96 hr. The excess *n*-propyl isocyanate and triethylamine were removed and the residue was dissolved in 15 ml of ethyl acetate. The ethyl acetate solution was filtered and 5 g of silica gel (80–200 mesh) was added to the filtrate. The ethyl acetate was removed *in vacuo* and 50 ml of benzene was added to the resin and evaporated *in vacuo* to remove the last traces of ethyl acetate. The dried silica gel with the reaction mixture adsorbed on it was added to the top of a silica gel column (60 × 2.5 cm), and the column was eluted with benzene at a rate of 4 ml/min. The product was eluted in the fractions between 500 and 600 ml. Aliquots of these fractions were chromatographed on tlc with benzene and only one spot (R_f 0.55) was observed. The benzene was removed from these fractions *in vacuo*. The resulting solid was recrystallized ($EtOH-H_2O$) to yield 0.363 g (44.4%) of product: mp 186–187°; ir (KBr) 1725, 1700 (C=O), 1168 cm^{-1} (SO_2); nmr ($CDCl_3$) 0.91 (t, 6, J = 7 Hz, CH_3), 1.63 (m, 4, $-CH_2-$), 3.75 (t, 4, J = 7 Hz, CH_2N), and 7.85 ppm (s, 4, aromatic).

Anal. Calcd for $C_{15}H_{18}IN_3O_5S$: C, 37.59; H, 3.79; N, 8.77. Found: C, 37.75; H, 3.83; N, 8.83.

Thermal Degradation of 1-(*p*-Iodobenzenesulfonyl)-3,5-di-*n*-propyl Isocyanurate (1).—A solution of 0.2 g (0.0004 mol) of **1** in 9.8 ml of dimethylformamide and 0.2 ml of water was heated at 170° for 48 hr. The solvent was removed *in vacuo*, and the residual oil was dissolved in 10 ml of 1 *N* NaOH. The pH of the solution was adjusted to 6 with HCl and a solid precipitated. The product was recrystallized (H_2O) to yield 0.06 g (71%) of 1,3-di-*n*-propyl isocyanurate (**2**): mp 137–138° (lit.[8] mp 138°); ir (KBr) 3200 (NH), 1730, 1710 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) M^+ 213 (41).

Registry No.—**1**, 35105-49-8.

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The Synthesis and Reactions of a Tetrachlorodioxopiperazine

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For a projected synthesis, we required the amino acid derivative *N*-trifluoroacetyl-α-chlorosarcosyl chloride (**2**). When we applied the usual two-step procedure[2] for the synthesis of α-chloroacyl chlorides to *N*-trifluoroacetylsarcosine (**1**), using first thionyl then sulfuryl chloride, we isolated the α,α-disubstituted sarcosyl chloride **3** (~18% yield) in some reactions. The unexpected instability of **3**[3] and the identification of

$CH_3N(TFA)CXX'COX''$

1, X = X′ = H; X″ = OH
2, X = H; X′ = Cl; X″ = Cl
3, X = X′ = X″ = Cl

(TFA = F_3CCO-)

several of its decomposition products as fully chlorinated or ketalized diketopiperazines seemed of sufficient interest to warrant this interim report, especially so since *N*-trifluoroacetyl-α-chlorosarcosyl chloride (**2**), which we obtained recently, is stable and does not yield diketopiperazines on standing.

As expected the ir spectrum of **3** showed acid chloride (1775 cm^{-1}) and trifluoroacetylamide (1660 cm^{-1}) carbonyl absorptions (CCl_4), the nmr spectrum displayed the *N*-methyl signals only slightly shifted from **1**, but the signal for the α hydrogen was absent. Finally the electron-impact mass spectrum with the highest *m/e* peak at 236 corresponds to the molecular ion of **3** less one chlorine atom, behavior which might be expected for a geminal halide.

On standing in a stoppered flask at room temperature for 24 hr, however, the original colorless liquid changed largely to a crystalline mass (mp 128–130°) whose ir spectrum now showed only one absorption (1728 cm^{-1}) in the carbonyl region and a single *N*-methyl signal (singlet, δ 3.51) in the nmr spectrum. An electron-impact mass spectrum showed as the highest peak *m/e* 243; the true parent ion (*m/e* 278) could be detected with chemiionization techniques.[4] These data and the elemental analysis ($C_6H_6N_2O_2Cl_4$) suggested the sarcosine anhydride structure **6** for this product.

The route to **6** starts with loss of trifluoroacetyl chloride from **3** to give the imidoyl chloride **4**, which, being a reactive bifunctional species, could dimerize *via* **5** (Scheme I). The addition of acyl halides to imines has precedents.[5] To prove that the distillate (**3**) still had an intact *N*-trifluoroacetyl linkage, a sample was refluxed with octadecylamine (**10**) in benzene. *N*-Trifluoroacetyloctadecylamine (**11**) was isolated in 62% yield, identical in all respects with a sample prepared from **10** and trifluoroacetic anhydride. Low temperature trapping experiments designed to demonstrate the presence of trifluoroacetyl chloride in decomposing samples of **3** have so far been unsuccessful.

The diketopiperazine **6** possessed appreciable reactivity, as might be expected.[6] The addition of 1 equiv of triethylamine to a slurry of **6** in methanol initiated a rapid exothermic reaction to produce a 1:3 mixture of the soluble mono- and diketals **7** and **8**, which were separated by fractional crystallization. The mono-

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