positions of the hydrogen atoms were calculated after preliminary refinement of the structure. In the final refinement anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy index is $R = 0.069$ for the 1409 observed reflections. A difference map has no peaks greater than ± 0.2 eÅ^{-3}.

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Registry No.—**1**, 38609-97-1; **2**, 59922-55-3; **3**, 59922-56-4; **4**, 59922-57-5; **5**, 1207-69-8; **6a**, 59922-58-6; **6b**, 59922-59-7; **7**, 59922-60-0; **8**, 59922-61-1; thionyl chloride, 7719-09-7; methylamine, 74-89-5; dodecylamine, 124-22-1; 9-chloroacridinium chloride, 19255-74-4; ethylene glycol, 107-21-1; dodecanol, 112-53-8.

Supplementary Material Available. Tables of the positional and thermal parameters for the structure of **2** (2 pages). Ordering information is given on any current masthead page.

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N-Arenesulfonyl Isocyanurates

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Several new synthetic methods are described for the preparation of *N*-mono- and bis(arenesulfonyl) substituted hexahydro-*s*-triazine-2,4,6-triones (isocyanurates). Base-catalyzed cycloaddition reactions of arenesulfonyl isocyanates and alkyl (aryl) isocyanates give exclusively 1-alkyl- (aryl-) 3,5-bis(arenesulfonyl) isocyanurates (**1**). Degradation of 1,3-dimethyl-5-phenyl-6,6-bis(dimethylamino)hexahydro-*s*-triazine-2,4-dione (**7**) with arenesulfonyl isocyanates leads to 1-methyl-3-phenyl-5-arenesulfonyl isocyanurates (**10**). Differently substituted **10** can also be synthesized from *N*-methyl-*N'*-arenesulfonylureas and aryl isocyanates in presence of base. Heating of arenesulfonamides and aryl isocyanates in presence of catalytic amounts of triethylamine yields 1,3-diaryl-5-arenesulfonyl isocyanurates (**11**).

Trisubstituted isocyanurates are readily obtained by base-catalyzed trimerization of alkyl and aryl isocyanates.[1] This reaction cannot be extended to arenesulfonyl isocyanates, because the initially formed dipolar 1:1 adducts with organic or inorganic bases do not undergo further reactions with excess sulfonyl isocyanates. Mixed oligomerizations of aryl or alkyl isocyanates with sulfonyl isocyanates leading to partially N-sulfonylated isocyanurates are also not known. Recently, 1-arenesulfonyl-3,5-dialkyl isocyanurates were obtained from the reaction of arenesulfonamides with alkyl isocyanates in the presence of triethylamine.[2,3] We now wish to report several routes for the convenient synthesis of N-persubstituted isocyanurates with one or two *N*-arenesulfonyl groups.

A. 1-Alkyl- (aryl-) 3,5-bis(arenesulfonyl)hexahydro-*s*-triazine-2,4,6-triones. In our investigations related to the selective stepwise oligomerization of isocyanates we studied the feasibility of base-catalyzed cotrimerizations of aryl as well as alkyl isocyanates with arenesulfonyl isocyanates. It is conceivable that the initially formed 1:1 adduct derived from arenesulfonyl isocyanate and certain heterocyclic tertiary amines would undergo reaction with alkyl or aryl isocyanates to yield 1,3-dialkyl- (aryl-) 5-arenesulfonyl or (and) 1-alkyl- (aryl-) 3,5-bis(arenesulfonyl) isocyanurates. Mixtures of alkyl or aryl isocyanates and arenesulfonyl isocyanates in molar ratios of 1:1 or 2:1 containing catalytic amounts of 1,2-dimethylimidazole (10–15 mol %)[4] solidify on standing at room temperature for a prolonged period of time (from 72 to 144 h). On workup of the crystalline reaction products with methanol, 1-alkyl- (aryl-) 3,5-bis(arenesulfonyl)hexahydro-*s*-triazine-2,4,6-triones **1a–e** are left behind undissolved in moderate to good yields (see Table I). The formation of the cotrimers **1**, derived from 2 mol of sulfonyl and 1 mol of alkyl or aryl isocyanate, seems to be independent of the molar ratio of the reactants since excess alkyl or aryl isocyanate did not alter the molar composition of the products.

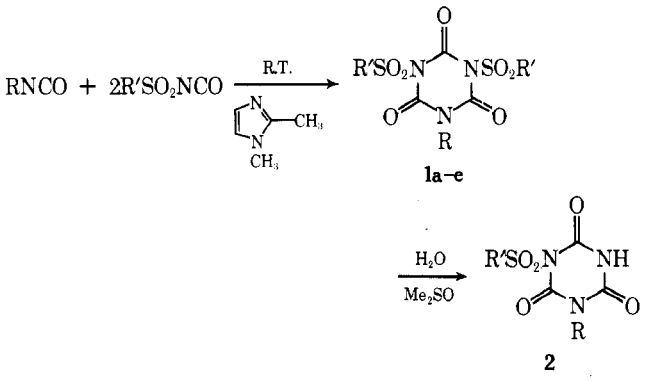
The isocyanurates of type **1** can be readily purified by reprecipitation from acetone–water. Attempted recrystallization of **1c** from dimethyl sulfoxide (Me_2SO)–water, however, leads to the hydrolytic removal of one of the *p*-toluenesulfonyl groups, giving 1-phenyl-3-(*p*-toluenesulfonyl)hexahydro-*s*-triazine-2,4,6-trione (**2**). The hydrolysis is best conducted by briefly heating a solution of **1c** in Me_2SO–water (volume ratio of 4:1) to 130 °C. The reaction can also be followed by monitoring the changes of the ^1H NMR spectrum of **1c** in wet Me_2SO-d_6 over a period of 60 min (at room temperature). The spectrum shows initially a singlet for the two protons of the two CH_3 groups of the *p*-tolyl moieties at δ 2.35 ppm. Slow disappearance of this signal and simultaneous appearance of

Table I. *N*-Sulfonyl Isocyanurates[a]

Compd	R	R′	Mp, °C	Yield, %	Reaction duration, h	Ir (C=O), cm^{-1} in $CHCl_3$, KBr[b]
1a	CH_3	*p*-ClC_6H_4	238	69	96	1720, 1700 (1740, 1715)
1b	CH_3	*p*-$CH_3C_6H_4$	217–218	40	96	1735, 1715 (1745, 1730, 1715)
1c	C_6H_5	*p*-$CH_3C_6H_4$	245	57	72	1740, 1720 (1735, 1715)
				75	144	
1d	C_6H_5	*p*-ClC_6H_4	241–243 dec	58	96	1735, 1725 (sh) (1735 broad)
1e	*p*-$CH_3C_6H_4$	*p*-ClC_6H_4	228–230	73	72	1740, 1730 (sh) (1740 broad)
1f	*m*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	238–239	80	3 months	1740, 1720
2	C_6H_5	*p*-$CH_3C_6H_4$	205	86		(1730 [sh], 1710)
10a	*p*-$CH_3C_6H_4$	C_6H_5	265–266	62[c]		1710 (1720, 1705)
				41[d]	120	
10b	*p*-ClC_6H_4	C_6H_5	260–265	86		1710 (1705, 1685)
10c	*p*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	235–237	38[e]	120	1715
11a	C_6H_5	C_6H_5	305	42	96	1730 (sh), 1720, 1700 (sh) (1730, 1710)
11b	*m*-$CH_3C_6H_4$	C_6H_5	284–285	35	96	1730 (sh), 1720, 1700 (sh) (1730 [sh], 1710)
11c	C_6H_5	*p*-$CH_3C_6H_4$	>300	49	96	1730 (sh), 1715, 1700 (sh) (1730 [sh], 1725, 1710)
11d	*m*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	288	27	64	1725 (sh), 1710, 1695 (sh) (1730 [sh], 1710)
11e	$C_6H_5CH_2$	*p*-$CH_3C_6H_4$	246–247	17[f]	120	1715, 1700
11f	*p*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	288	28[g]	140	1720 (broad)

[a] Satisfactory analytical values (±0.3% for C, H, N) were reported for all compounds. Ed. [b] Values in parentheses in KBr. [c] From compound **7** and *p*-toluenesulfonyl isocyanate. [d] From *N*-methyl-*N*′-(*p*-toluenesulfonyl)urea and phenyl isocyanate. [e] From *N*-methyl-*N*′-(*p*-toluenesulfonyl)urea and *p*-tolyl isocyanate. [f] From *N*-phenyl-*N*′-(*p*-toluenesulfonyl)urea and benzyl isocyanate. [g] From *N*-phenyl-*N*′-(*p*-toluenesulfonyl)urea and *p*-tolyl isocyanate.

a new singlet at δ 2.30 ppm, indicating the transformation **1c** → **2**, can be observed within minutes. Since no other CH_3 signal is visible in the spectrum the methyl group of the by-product, *p*-toluenesulfonic acid, must be hidden underneath the new signal. A similar hydrolytic removal of a *N*-arenesulfonyl group has been reported for 1-(*p*-iodobenzenesulfonyl)-3,5-di-*n*-propyl isocyanurate.[2]

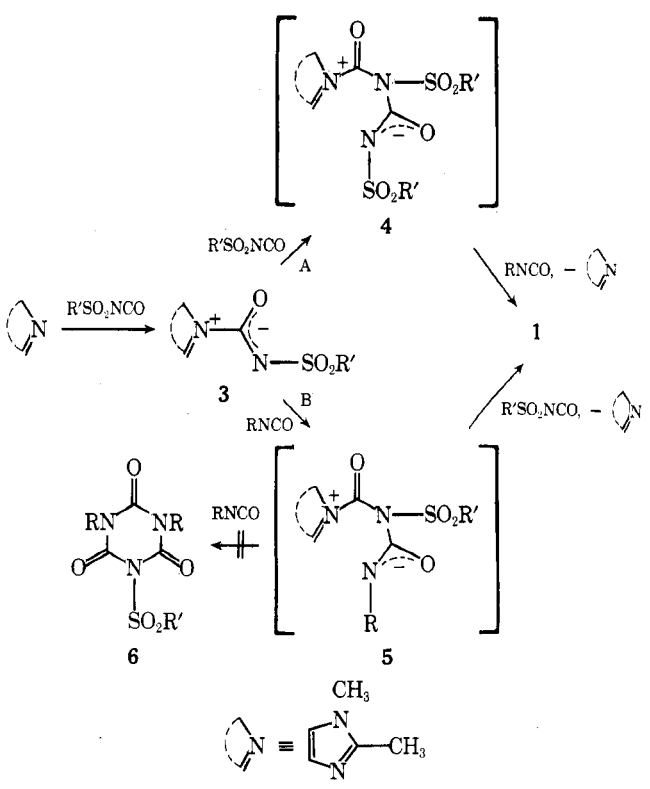


It is assumed that the cotrimers **1a–e** are products derived via a sequence of reactions involving dipolar intermediates (Scheme I). Initially a dipolar sulfonyl isocyanate–catalyst adduct **3** is formed, which can be intercepted either by a second molecule of sulfonyl isocyanate to give **4** or by alkyl (aryl) isocyanate, giving **5**. Further reaction of these dipoles with more isocyanate—sulfonyl or alkyl (aryl)—as indicated followed by expulsion of the catalyst produces the cotrimers **1**.

That adducts of type **3** are formed as initial products could be verified by independent experiments. Mixing equimolar quantities of *p*-toluenesulfonyl isocyanate and 1,2-dimethylimidazole in acetone produces instantaneously **3** (R′ = *p*-$CH_3C_6H_4$) in 93% yield. Changing the molar ratio from 1:1 to 2:1 with sulfonyl isocyanate in excess or adding 1 mol of phenyl isocyanate to the mixture does not interfere with the initial formation of **3**. Similar adducts are known to be formed from other nitrogen bases and sulfonyl isocyanates.[5,6]

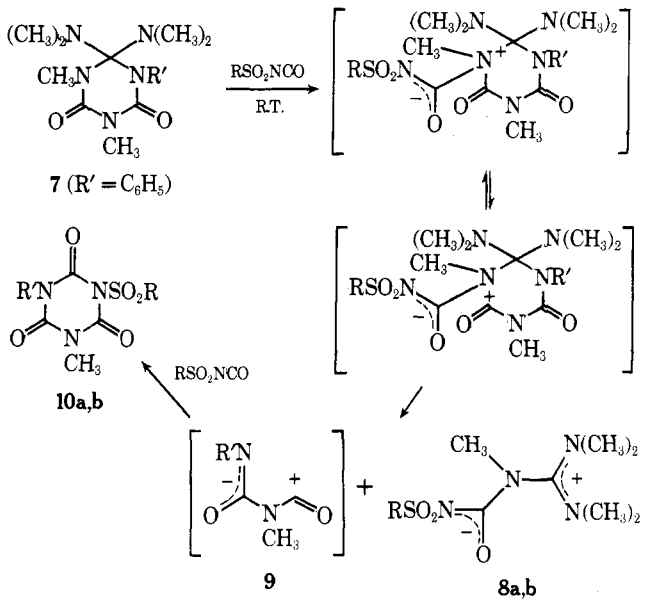
Attempts to oligomerize *p*-toluenesulfonyl isocyanate alone leading to either the unknown dimer or trimer failed. No

Scheme I



changes could be observed in the ir spectra of a sample of the isocyanate containing only catalytic amounts of 1,2-dimethylimidazole, which was kept for 30 days at room temperature. This observation could indicate that the 1:1 adducts **3** are not intercepted by excess arenesulfonyl isocyanate (which would lead to **4**) but rather by aryl isocyanate, giving **5**. In the next step, leading to **1**, however, the preference of the dienophile attack at the dipole **5** is again reversed since no isocyanurates **6**, derived from 2 mol of alkyl (aryl) isocyanate and 1 mol of sulfonyl isocyanate, are obtained in these reactions. The exclusive formation of type **1** isocyanurates was also

Scheme II



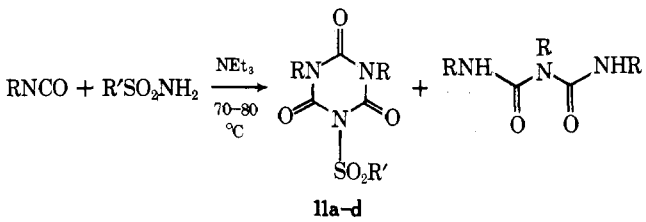
demonstrated in an experiment in which an equimolar mixture of *p*-toluenesulfonyl and *m*-tolyl isocyanate and catalytic amounts of 1,2-dimethylimidazole was kept for 3 months at room temperature. Workup with methanol gave an 80% crude yield of **1f** but no corresponding **6** (R = *m*-$CH_3C_6H_4$).[7] Analytical data and yields of all the new isocyanurates **1a–f** are listed in Table I.

B. 1-Alkyl-3-aryl-5-(arenesulfonyl)hexahydro-*s*-triazine-2,4,6-triones. Isocyanurates, derived from 1 mol of alkyl, aryl, and arenesulfonyl isocyanate, each can be prepared by treating a solution of 1,3-dimethyl-5-phenyl-6,6-bis(dimethylamino)hexahydro-*s*-triazine-2,4-dione (**7**)[8] with 2 mol of arenesulfonyl isocyanate at room temperature. The new isocyanurates **10** precipitate within minutes from the reaction mixtures in good yield. Dipolar adducts of type **8**[6] composed of 1 mol of pentamethylguanidine and arenesulfonyl isocyanate are obtained as side products (**8a** with R = *p*-$CH_3C_6H_4SO_2$ could be isolated in 52% yield in the reaction of **7** with *p*-toluenesulfonyl isocyanate). We also attempted to synthesize the cotrimers **10** by mixing the three parent isocyanates, i.e., methyl, phenyl, and *p*-toluenesulfonyl isocyanate but did not observe any reaction (as followed by ir) even after standing for 24 h. Addition of small amounts of pentamethylguanidine to the mixture did not catalyze the oligomerization, thus eliminating the possible formation of **8** and **10** from dissociation products of **7** (methyl and phenyl isocyanate).

It is more likely that the formation of **8** and **10** from **7**, which involves degradation and re-formation of a *s*-triazine ring, proceeds via cleavage of the C–N bond at positions 2–3 after attack of arenesulfonyl isocyanate. Further possible reaction steps are outlined in Scheme II.

This reaction is related to similar displacements of one dipolarophile by another in cycloadducts derived from isocyanates and isoquinoline as described by Huisgen and coworkers.[9]

C. 1,3-Diaryl-5-(arenesulfonyl)hexahydro-*s*-triazine-2,4,6-triones. In extending the reported synthesis of N-sulfonylated isocyanurates from arenesulfonamides and alkyl isocyanates in the presence of triethylamine[2,3] to aryl isocyanates we were able to obtain 1,3-diaryl-5-arenesulfonylhexahydro-*s*-triazine-2,4,6-triones **11a–d** in moderate yield

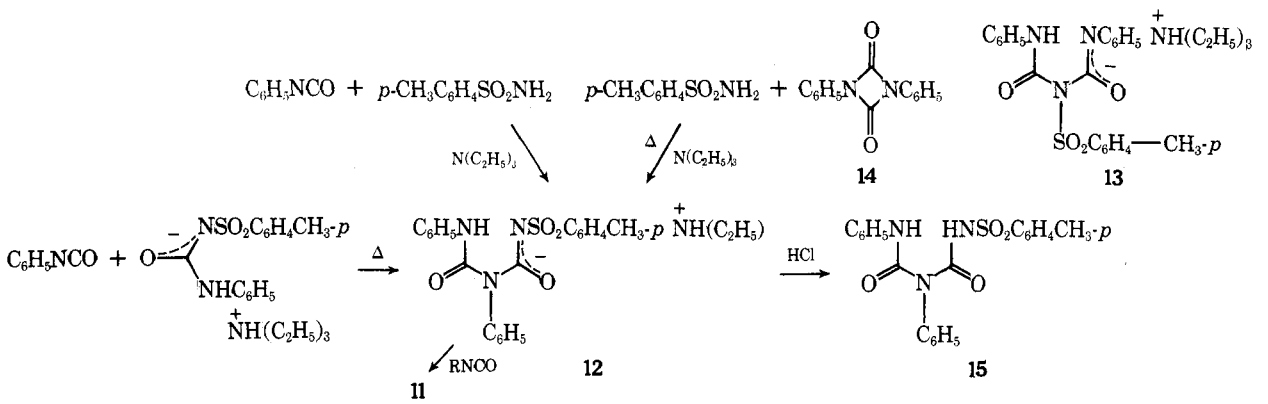


(see Table I for yields). By-products in these reactions, which are carried out by heating sulfonamides with excess aryl isocyanate and catalytic amounts of triethylamine for 64–96 h to 70–80 °C, are *N,N',N''*-triarylbiurets.

When a mixture of equimolar amounts of *p*-toluenesulfonamide and triethylamine in excess phenyl isocyanate is kept at room temperature for several hours, a precursor of the expected isocyanurates with a molar composition of 1:2:1 (*p*-toluenesulfonamide:phenyl isocyanate:triethylamine) is obtained in nearly quantitative yield. This intermediate was found to be the triethylammonium salt of *N,N'*-diphenyl-*N''*-(*p*-toluenesulfonyl)biuret **12**. Compound **12** can also be prepared in 43% yield on heating a chloroform solution of equimolar amounts of 1,3-diphenyldiazetidine-2,4-dione **14**, *p*-toluenesulfonamide, and triethylamine for 23 h. A mixture of **14** and *p*-toluenesulfonamide heated in the absence of triethylamine in chloroform remains unchanged while carbanilide and *N,N*-dimethyl-*N'*-(*p*-toluenesulfonyl)formamidine are obtained in dimethylformamide at 120 °C. The biuret salt **12** is also produced in 54% yield on heating the triethylammonium salt of *N*-phenyl-*N'*-(*p*-toluenesulfonyl)urea with equimolar amounts of phenyl isocyanate for 4 h in chloroform (see Scheme III).

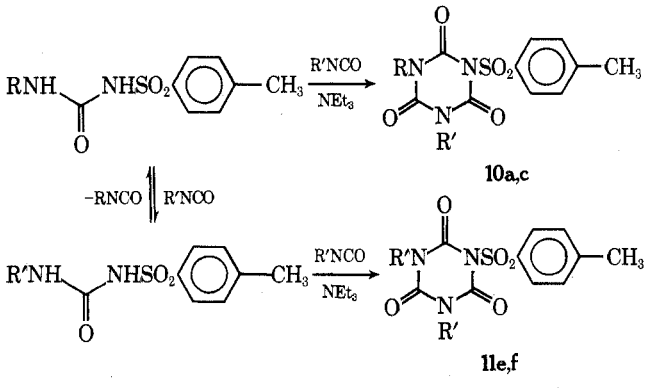
The free *N,N'*-diphenyl-*N''*-(*p*-toluenesulfonyl)biuret **15** is formed in 90% yield on treating a methylene chloride solution of **12** with hydrogen chloride. The proposed asymmetric structure of the biuret **15** and its salt **12** was confirmed by ^{13}C NMR spectroscopy. A spectrum of **15** in $CDCl_3$ showed two distinctly different carbonyl carbons at δ 153.3 and 150.4 ppm, thus eliminating the symmetric formula **13** for the reaction product.

Scheme III



The biuret **15** can readily be converted in 52% yield into **11c** on heating with excess phenyl isocyanate and a catalytic amount of triethylamine at 75 °C for 96 h. Using the triethylammonium salt **12** in a similar reaction led to about 10% **11c** after 15 h reaction duration while most of the excess phenyl isocyanate was trimerized under the influence of triethylamine.

The stepwise formation of isocyanurates of type **11** via *N*-arenesulfonylureas and biurets allows also the synthesis of isocyanurates with three different substituents. If *N*-methyl-*N'*-(*p*-toluenesulfonyl)urea is heated with excess phenyl isocyanate and catalytic amounts of triethylamine to 80 °C for 120 h, 1-methyl-3-phenyl-5-(*p*-toluenesulfonyl)-isocyanurate (**10a**) is obtained in 41% yield. Similarly, **10c** is obtained on heating the same urea with *p*-tolyl isocyanate (38% yield). On heating *N*-phenyl-*N'*-(*p*-toluenesulfonyl)urea with excess of either benzyl or *p*-tolyl isocyanate and triethylamine, however, not the expected **10d** and **10e** but rather **11e** and **11f** were obtained in low yields (17 and 23%, respectively).



Their formation can readily be explained by an exchange of substituents in the urea during heating with excess benzyl or *p*-tolyl isocyanate.

Experimental Section[10]

General Procedure for the Preparation of 1-Alkyl- (aryl-) 3,5-bis(arenesulfonyl)hexahydro-*s*-triazine-2,4,6-triones 1a–f. On adding 0.02 mol of 1,2-dimethylimidazole to a mixture of 0.16 mol of alkyl (or aryl) isocyanate and 0.16 mol of arenesulfonyl isocyanate, a colorless precipitate was formed instantaneously which was redissolved on gentle heating of the suspension. The reaction mixtures solidified on standing at room temperature for prolonged periods of time. The resulting crystal cake was taken up in ca. 70 ml of methanol and filtered, and the residue was washed with methanol and finally with diethyl ether leaving the isocyanurates as colorless crystals. Samples were recrystallized for analysis from acetone–water or acetone–methanol; the spectral data are given in Table I.

1-Phenyl-3-(*p*-toluenesulfonyl)hexahydro-*s*-triazine-2,4,6-trione (2). A suspension of 2.0 g (0.0039 mol) of **1c** in 4 ml of dimethyl sulfoxide and 1 ml of water was placed into a preheated oil bath at 130 °C. A clear solution was formed almost immediately from which colorless crystals precipitated within a few minutes. The reaction was stopped after 5 min, the mixture cooled and filtered, and the residue washed with water, leaving 1.2 g (86%) of **2**, mp (from acetone–water) 205 °C.

1,2-Dimethyl-3-(*p*-toluenesulfocarbamoyl)imidazolium Inner Salt 3 (R' = *p*-$CH_3C_6H_4$). On mixing 0.96 g (0.01 mol) of 1,2-dimethylimidazole and 2.00 g (0.01 mol) of *p*-toluenesulfonyl isocyanate in ca. 25 ml of acetone, colorless crystals were precipitated at once while the mixture became warm. After standing for 30 min, the precipitate was collected and washed with acetone and finally diethyl ether; 2.75 g (93%) of **3** was obtained as colorless plates, mp 155 °C dec.

Anal. Calcd for $C_{13}H_{15}N_3O_3S$: C, 53.24; H, 5.16; N, 14.33. Found: C, 53.01; H, 5.24; N, 14.18.

The dipolar adduct can also be obtained from similar reaction mixtures containing either larger amounts of *p*-toluenesulfonyl isocyanate (0.02 mol, 90% yield of **3**) or 0.01 mol of phenyl isocyanate (88% yield of **3**).

1-Methyl-3-phenyl-5-(*p*-toluenesulfonyl)hexahydro-*s*-triazine-2,4,6-trione (10a). A. From 1,3-Dimethyl-5-phenyl-6,6-bis(dimethylamino)hexahydro-*s*-triazine-2,4-dione (7) and *p*-Toluenesulfonyl Isocyanate. An exothermic reaction took place on gradually adding 3.90 g (0.02 mol) of *p*-toluenesulfonyl isocyanate to a solution of 3.05 g (0.01 mol) of 1,3-dimethyl-5-phenyl-6,6-bis-(dimethylamino)hexahydro-*s*-triazine-2,4-dione (**7**)[8] in 25 ml of chloroform. Colorless crystals of **10a** precipitated on cooling the solution to −5 °C for 18 h; filtration yielded 2.3 g (62%) of **10a**, recrystallized for analysis from acetone–water. Colorless crystals of **8a** (R = *p*-$CH_3C_6H_4$) were deposited on diluting the chloroform filtrate with diethyl ether: 1.7 g (52%); mp 210–217 °C dec (from methylene chloride–diethyl ether); ir ($CHCl_3$) 1650, 1605 cm^{-1} (C=N and C=O bands).

Anal. Calcd for $C_{14}H_{22}N_4O_3S$: C, 51.52; H, 6.80; N, 17.17; S, 9.82. Found: C, 51.54; H, 6.75; N, 17.24; S, 9.84.

The isocyanurate **10b** was prepared similarly. In this case the corresponding **8b** was not isolated from the reaction mixture.

B. From *N*-Methyl-*N'*-(*p*-toluenesulfonyl)urea and Phenyl Isocyanate. A mixture of 9.12 g (0.04 mol) of *N*-methyl-*N'*-(*p*-toluenesulfonyl)urea, 24.0 g (0.2 mol) of phenyl isocyanate, and 1.0 g (0.01 mol) of triethylamine was heated under exclusion of air to 80 °C for 120 h. Crystals started to separate from the initially clear reaction solution. Unreacted isocyanate was removed under vacuum, and the crystalline residue was triturated with methanol. Filtration gave a mixture of **10a** and *N,N',N''*-triphenylbiuret (15.0 g). The crude mixture was dissolved in hot chloroform and on dilution with methanol, 6.1 g (41%) of **10a** precipitated in the form of colorless crystals, identical in mixture melting point and ir with **10a** obtained under A. On concentrating the filtrate, 4.0 g of *N,N',N''*-triphenylbiuret can be isolated. Isocyanurate **10c** (R = R' = *p*-$CH_3C_6H_4$) was prepared similarly using *p*-tolyl isocyanate; yields are given in Table I.

General Procedure for the Preparation of 1,3-Diaryl-5-(arenesulfonyl)hexahydro-*s*-triazine-2,4,6-triones 11a-d. Mixtures consisting of 0.2 mol of aryl isocyanate, 0.04 mol of arenesulfonamide, and 0.01 mol of triethylamine were heated to 70–80 °C for a prolonged period of time, resulting in the nearly complete solidification of the flask content. The crude products were treated with methanol and filtered, leaving mixtures of the isocyanurate **11** and the corresponding *N,N',N''*-triarylbiuret. Satisfactory separation of the two components was possible by dissolving the crude products in hot chloroform and treating the solutions with approximately double the volume of methanol, causing a nearly quantitative precipitation of the isocyanurate, very often analytically pure, while the biurets remained dissolved. The crude isocyanurates can be recrystallized from acetone–water or chloroform–methanol. The biurets crystallized on concentrating the filtrates and were purified by recrystallization from methanol.

Isocyanurate 11c from *N,N'*-Diphenyl-*N''*-(*p*-toluenesulfonyl)biuret 15 and Phenyl Isocyanate. A mixture of 1.0 g (0.0025 mol) of **15**, 2.0 g (0.017 mol) of phenyl isocyanate, and 0.1 g of triethylamine was heated for 96 h to 75 °C. The partially solidified reaction product was triturated with methanol, and the undissolved colorless crystals were filtered off and washed with methanol. The crude product, 1.0 g of a mixture of **11c** and some *N,N',N''*-triphenylbiuret (ir), was treated with boiling methanol, leaving 0.55 g (52%) of pure **11c** undissolved. The material was identical in ir comparison with **11c** prepared according to the above procedure. Concentration of the filtrate yielded *N,N',N''*-triphenylbiuret.

Isocyanurates 11e and 11f from *N*-Phenyl-*N'*-(*p*-toluenesulfonyl)urea and Benzyl or *p*-Tolyl Isocyanate. Colorless precipitates were formed on heating a mixture of 0.02 mol of *N*-phenyl-*N'*-(*p*-toluenesulfonyl)urea and 0.1 mol of benzyl or *p*-tolyl isocyanate for 120 h to 80 °C. After most of the excess isocyanates were removed by vacuum distillation the residues were triturated with methanol, and the crude mixtures of isocyanurate and the corresponding N,N',N''-trisubstituted biuret were dissolved in hot chloroform. The isocyanurates can be precipitated from the solutions by adding methanol; yields are in Table I. On concentration of the filtrates the corresponding trisubstituted biurets can be isolated.

***N,N'*-Diphenyl-*N''*-(*p*-toluenesulfonyl)biuret 15 and Its Triethylammonium Salt 12. A. From Phenyl Isocyanate and *p*-Toluenesulfonamide.** A mixture of 3.40 g (0.02 mol) of *p*-toluenesulfonamide, 12.0 g (0.1 mol) of phenyl isocyanate, and 2.0 g (0.02 mol) of triethylamine was kept at room temperature for 18 h. The initially clear reaction mixture became warm, and colorless crystals separated on standing. The formed suspension was diluted with diethyl ether, and the crystals were filtered off and washed with ether, leaving 4 g (92%) of **12**, mp 129–131 °C dec (from $CHCl_3$–diethyl ether); ir ($CHCl_3$) 1680 cm^{-1} (C=O).

Anal. Calcd for $C_{27}H_{34}N_4O_4S$: C, 63.51; H, 6.71; N, 10.97. Found: C, 63.45; H, 6.53; N, 10.96.

The free biuret **15** was obtained on treating a solution of 10.20 g (0.02 mol) of **12** in 50 ml of dichloromethane with dry hydrogen chloride gas for 1 h. The residue obtained after evaporating the solvent was treated with methanol leaving colorless plates of **15**, which were filtered off and washed with methanol: 7.4 g (90%) of **15**; mp 140 °C (MeOH); ir ($CHCl_3$) 1720, 1680 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) δ 153.3 and 150.4 ppm (carbonyl C).

Anal. Calcd for $C_{21}H_{19}N_3O_4S$: C, 61.61; H, 4.68; N, 10.27. Found: C, 61.09; H, 4.76; N, 10.13.

B. From 1,3-Diphenyldiazetidine-2,4-dione (14) and *p*-Toluenesulfonamide. A solution of 0.01 mol of **14**, *p*-toluenesulfonamide, and triethylamine each in 25 ml of chloroform was kept at 80 °C for 23 h while the progress of the reaction was followed by ir (disappearance of C=O bands of the diazetidine-2,4-dione at 1770 cm^{-1}). The salt **12** was separated from the reaction solution by adding diethyl ether. Thus 2.2 g (43%) of **12** was obtained, identical with a sample prepared under A.

A mixture of 0.01 mol of **14** and *p*-toluenesulfonamide was heated in 10 ml of DMF for 20 h to 120 °C, while the disappearance of **14** was followed by ir. The resulting brown solution yielded, on gradual dilution with water, fractions of 2.2 g of *N,N'*-diphenylurea, mp 245 °C (identical in ir comparison with an authentic sample), and 0.9 g of *N,N*-dimethyl-*N'*-(*p*-toluenesulfonyl)formamidine, mp 134–135 °C (lit.[11] 135–137 °C), ir ($CHCl_3$) 1625 cm^{-1} (C=N).

C. From *N*-Phenyl-*N'*-(*p*-toluenesulfonyl)urea and Phenyl Isocyanate. On adding 0.4 g (0.004 mol) of triethylamine to a suspension of 1.1 g (0.0038 mol) of *N*-phenyl-*N'*-(*p*-toluenesulfonyl)urea in 10 ml of chloroform, salt formation with solvation of the starting material takes place. After 0.45 g (0.0038 ml) of phenyl isocyanate was added the solution was heated to reflux for 3–4 h while the progress of the reaction was followed by ir (disappearance of the –N=C=O band at 2260 cm^{-1}). The resulting solution was diluted with diethyl ether, causing separation of 1.05 g (54%) of **12**, identical with a sample prepared under A.

Registry No.—**1a**, 59812-63-4; **1b**, 59812-64-5; **1c**, 59812-65-6; **1d**, 59812-66-7; **1e**, 59812-67-8; **1f**, 59812-68-9; **2**, 59812-69-0; **3** (R' = *p*-$CH_3C_6H_4$), 59812-79-2; **7**, 59812-80-5; **10a**, 59812-70-3; **10b**, 59812-71-4; **10c**, 59812-72-5; **11a**, 59812-73-6; **11b**, 59812-74-7; **11c**, 59812-75-8; **11d**, 59812-76-9; **11e**, 59812-77-0; **11f**, 59812-78-1; **12**, 59812-82-7; **14**, 1025-36-1; **15**, 59812-81-6; RNCO (R = Me), 624-83-9; RNCO (R = Ph), 103-71-9; RNCO (R = *p*-$CH_3C_6H_4$), 622-58-2; RNCO (R = *m*-$CH_3C_6H_4$), 621-29-4; RNCO (R = *p*-ClC_6H_4), 104-12-1; RNCO (R = $PhCH_2$), 3173-56-6; R'SO_2NCO (R' = *p*-ClC_6H_4), 5769-15-3; R'O_2NCO (R' = *p*-$CH_3C_6H_4$), 4083-64-1; R'SO_2NH_2 (R' = Ph), 98-10-2; R'SO_2NH_2 (R' = *p*-$CH_3C_6H_4$), 70-55-3; 1,2-dimethylimidazole, 1739-84-0; *N*-methyl-*N'*-(*p*-toluenesulfonyl)urea, 13909-69-8; *N*-phenyl-*N'*-(*p*-toluenesulfonyl)urea, 13909-63-2; *N,N'*-diphenylurea, 102-07-8.

References and Notes

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Fluoroxytrifluoromethane Reactions with Polynuclear Arenes. A New Route to Fluorinated K-Region Ketones

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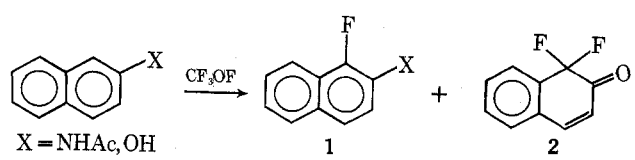
Reactions between 9-(*N*-acetylamino)phenanthrene (**3**), 5-(*N*-acetylamino)benzo[*c*]phenanthrene (**5**), 5-methoxy-7,12-dimethylbenz[*a*]anthracene (**7**), and fluoroxytrifluoromethane (CF_3OF) yielded 10,10-difluorophenanthren-9(10*H*)-one (**4**, 40%), 6-fluorobenzo[*c*]phenanthren-5(6*H*)-one (**6**, 30%), and 6-fluoro-7,12-dimethylbenz[*a*]anthracen-5(6*H*)-one (**8**, 45%), respectively, as the major products. Compounds **6** and **8** were found to exist predominantly as the K-region ketone instead of the usual K-region phenol; steric and fluorine electronic effects are used to explain the preference for the ketonic tautomer.

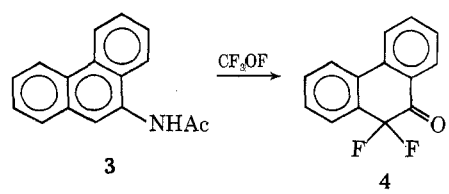
Previous work on fluoroxytrifluoromethane (CF_3OF) reactions with polynuclear aromatic systems has revealed reactions which include monofluorination, *gem*-difluorination, and oxidation.[2] Thus certain 2-substituted naphthalene derivatives reacted with CF_3OF to produce 1-fluoro substituted naphthalenes (**1**) and 1,1-difluoronaphthalen-2(1*H*)-one (**2**).



9-Substituted anthracenes produced only the oxidation product anthraquinone. Further studies of CF_3OF reactions with higher polynuclear arenes were pursued to determine (1) the orientation and extent of fluorination, (2) the synthetic utility, and (3) the properties of the derived products.

Results

9-(*N*-Acetylamino)phenanthrene (**3**) reacted with CF_3OF in chloroform solution at room temperature to yield a mixture of 9,10-phenanthraquinone (3%), 10,10-difluorophenanthren-9(10*H*)-one (**4**, 40%), and an unidentified high-melting



material. No evidence was obtained for the presence of a monofluorination product. The *gem*-difluoro ketone **4** shows carbonyl absorption in the infrared spectrum at 1700 cm^{-1}; compound **2** had previously been observed to contain absorption at 1700 cm^{-1} for the carbonyl group.[2]