Anal. Calcd for M·+ (determined by high-resolution exact-mass measurements): 435.1074. Found: 435.10323.

Compound **5c:** mp 163–165 °C; $^1$H NMR ($CDCl_3$) δ 2.38 (s, 3 H, p-$CH_3$), 5.13 (s, 2 H, benzyl $CH_2$), 6.68–7.60 (m, 12 H), and 7.73 (d, 2 H); mass spectrum *m/e* (rel intensity) 423 (4), 422 (8), 421 (36, M·+), 356 (2, M·+ − $SO_2$ − H), 268 (3), 267 (10), 266 (62, M·+ − Ts), 234 (1, M·+ − Ts − S), 181 (2), 165 (2), 91 (100).

Anal. Calcd for $C_{22}H_{19}N_3O_2S_2$ (421): C, 62.71; H, 4.51; N, 9.98. Found: C, 62.66; H, 4.70; N, 10.05.

Compound **5d:** mp 143–144 °C; $^1$H NMR ($CDCl_3$) δ 2.38 (s, 3 H, p-$CH_3$), 3.79 (s, 3 H, p-$OCH_3$), 5.13 (s, 2 H, benzyl $CH_2$), 6.73–7.36 (m, 11 H), and 7.69 (d, 2 H); mass spectrum *m/e* (rel intensity) 453 (4), 452 (8), 451 (38, M·+), 386 (2, M·+ − $SO_2$ − H), 298 (3), 297 (8), 296 (48, M·+ − Ts), 264 (1, M·+ − Ts − S), 190 (2), 91 (100).

Anal. Calcd for $C_{23}H_{21}N_3O_3S_2$ (451): C, 61.20; H, 4.66; N, 9.31. Found: C, 61.20; H, 4.95; N, 9.19.

For the independent synthesis of **5c**, the procedure of Goerdeler et al.[4] was utilized to prepare **7**. This compound (1.3 g) was dissolved in dry benzene (20 ml) containing 0.4 g of pyridine. An equimolar amount of tosyl chloride (0.95 g) was added dropwise with stirring and the reaction mixture was left overnight at room temperature. The precipitate (PyHCl) was filtered off and the filtrate was evaporated in vacuo to give a solid (**5c**, 76%) which was crystallized from methanol.

**Basic Hydrolysis of 5c.** Compound **5c** (4.2 g) was dissolved in a 2.4 M solution of KOH in ethanol (200 ml). The solution was refluxed for 2 h, then poured into ice–water (100 ml) and acidified with 2 N aqueous hydrochloric acid. The precipitate (*N*-benzyl-*N'*-tosylurea)[1] was isolated and dried in vacuo at 70 °C, yield 92%, mp 178–180 °C. The mother liquor was extracted twice with ether and the extracts were dried and then evaporated to give benzoic acid in 82% yield.

**Crystal Structure Determination of 5c.** Crystal data: $C_{22}H_{19}N_3O_2S_2$ (421.54); monoclinic, $a$ = 10.049 (5), $b$ = 19.985 (3), $c$ = 10.526 (5) Å, $\beta$ = 107.97 (3), $d_m$ = 1.39 (1) g cm$^{-3}$, $d_c$ ($Z$ = 4) = 1.392 g cm$^{-3}$, $\mu$ (Cu K$\alpha$) = 25.17 cm$^{-1}$. Systematic absences $0k0$ for $k$ odd and $h0l$ for $l$ odd establish the space group as $P2_1/c$. Intensity data from a crystal 0.33 × 0.30 × 0.14 mm were collected for a quarter of reciprocal space out to $2\theta$ = 144° with graphite-monochromatized Cu K$\alpha$ radiation ($\lambda$ = 1.54178 Å) using a Nonius CAD-4 diffractometer in the $\theta$–$2\theta$ mode; 3941 independent reflections were measured of which 883 had $I < 3\sigma(I)$ and were considered as unobserved. The data were corrected for absorption by the method of Busing and Levy[11] and for the usual geometric and polarization factors. The structure was solved by direct methods. Hydrogen atoms were located by the use of difference Fourier techniques. The structure was refined with individual isotropic temperature factors for the hydrogen atoms, individual anisotropic temperature factors for all other atoms, and correction for anomalous dispersion of the sulfur atoms to a final $R$ value of 3.9% for the observed reflections. All computations were carried out using the local version of the x-ray 72 program system.[12]

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**Registry No.**—**1**, 42770-61-6; **4a**, 59938-44-2; **4b**, 59938-45-3; **4c**, 59938-46-4; **4d**, 59938-47-5; **5a**, 59938-48-6; **5b**, 59938-49-7; **5c**, 59938-50-0; **5d**, 59938-51-1; **7**, 59938-52-2; RCH=NR' (R = $C_6H_5$; R' = $CH_3$), 622-29-7; RCH=NR' (R = $C_6H_5$; R' = p-$ClC_6H_4$), 15383-71-8; RCH=NR' (R = p-$NO_2C_6H_4$; R' = p-$ClC_6H_4$), 25105-56-0; RCH=NR' (R = R' = p-$MeOC_6H_4$), 3261-60-7; RC≡N (R = $CH_3$), 75-05-7; RC≡N (R = $C_6H_5CH_2$), 140-29-4; RC≡N (R = $C_6H_5$), 100-47-0; RC≡N (R = p-$MeOC_6H_4$), 874-90-8.

**Supplementary Material Available.** Tables of bond lengths and angles and final atomic parameters of **5c** (5 pages). Ordering information is given on any current masthead page.

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# Structure and Reactions of an Unusual Thionyl Chloride Oxidation Product. 9-Chloroacridinium 2-Chloro-1-(chlorosulfinyl)-2-oxoethylide

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9-Oxo-10-acridanacetic acid (1) reacts with thionyl chloride to give the title compound (2) in 95% yield. The structure **2** is established by x-ray crystallography. Exposures of **2** to amines, alcohols, and water indicate that, in addition to the anticipated reactions at the acyl chloride and the 9-chloroacridinium sites, the chlorosulfinyl group of **2** is readily cleaved. Controlled methanolysis, however, afforded the unstable thioamide *S*-oxide **7**. Pyrolysis of **2** leads to 9-chloroacridine.

9-Oxo-10-acridanacetic acid (**1**)[1] is a compound of some interest as an antiviral agent.[2] In the course of derivatization of **1**, we attempted to prepare the corresponding acid chloride by treatment with thionyl chloride. The dissolution of **1** ($C_{15}H_{11}NO_3$) with thionyl chloride in refluxing 1,2-dimethoxyethane was followed by crystallization of a copious amount (95%) of crimson red prisms, mp 206–208 °C, having the elemental composition of $C_{15}H_8Cl_3NO_2S$. We wish to record the structure (**2**) and reactions of this unusual intermediate.

The structure **2** has been determined by x-ray crystallography, details of which are described below. A stereodrawing

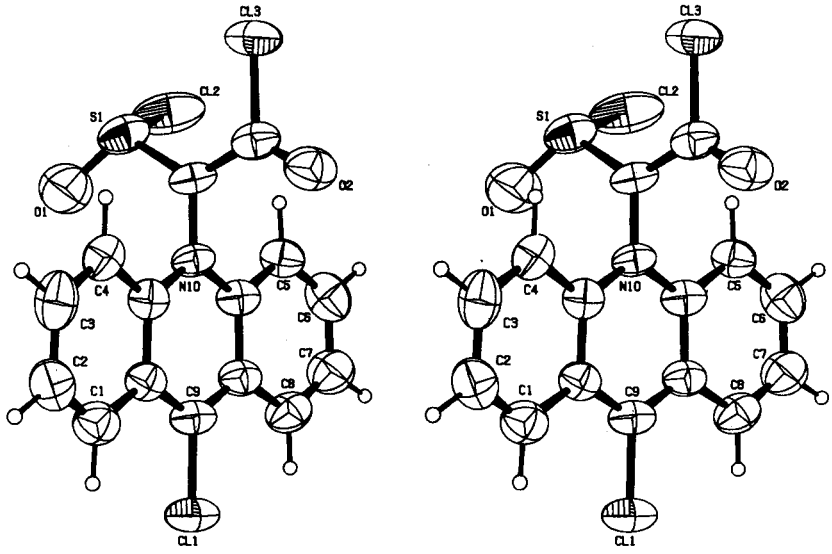
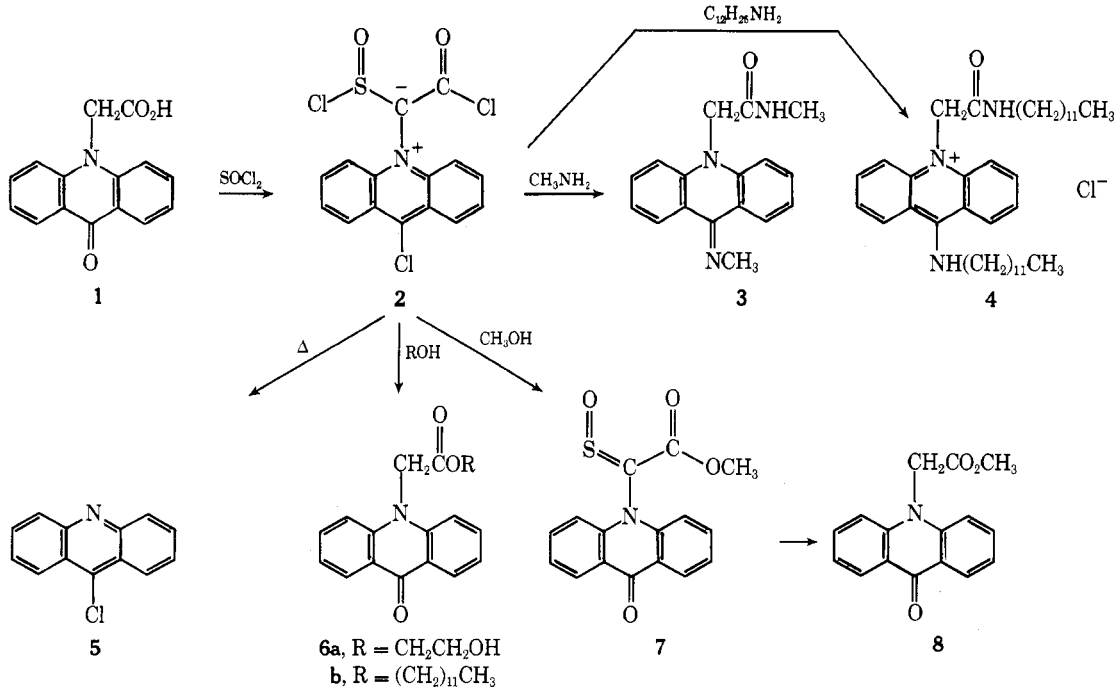



**Figure 1.** A stereoscopic drawing of a molecule of **2**. The thermal ellipsoids are scaled to the 50% probability level and the hydrogen atoms are shown as spheres of an arbitrary size.

of **2** (Figure 1) and some bond lengths and bond angles are also given. Apparently in addition to the formation of acid chloride function, thionyl chloride has reacted with 9-oxo-10-acridanacetic acid (**1**) at two additional sites as shown in structure **2**. The conversion of 10-alkyl-9-acridanone to 10-alkyl-9-chloroacridinium salts with thionyl chloride is known.[3] The sulfinylation of the methylene group is more interesting. Similar oxidizing reactions of thionyl chloride are known in the literature.[4] Although $\alpha$-chlorosulfinyl species such as **2** have been proposed[4b,c] as initial intermediates in complex oxidative reaction sequences involving carboxylic acids and thionyl chloride, such sulfinyl chlorides have not been isolated in these reactions. The isolation is possible here probably owing to the crystallization of the stable ylide, in the absence of nucleophiles.

The carbon–sulfur bond in **2** was found to be very readily cleaved by protonic reagents. Thus on reaction with methylamine, dodecylamine, ethylene glycol, and dodecanol, followed by brief exposure of the reaction mixtures to water during isolation of the products, the chlorosulfinyl group of **2** is readily lost in forming amides and esters of the acridanacetic acids **3**, **4**, **6a**, and **6b**, respectively. Under mild methanolysis conditions, we were able to isolate the unstable methyl 9-oxo-$\alpha$-sulfinyl-10-acridanacetate (**7**). The sulfinyl group in **7**, however, was readily cleaved by mild hydrolysis to afford **8**. Compound **7** appears to be a rare example of an $\alpha$-carbonyl-substituted[5] thioamide *S*-oxide.[6,7] Owing to the instability of **7**, we have not investigated the stereochemistry of the substituents on the sulfur atom. The presence of strong bands at 1173 and 1085 $cm^{-1}$ in the infrared spectrum of **7** is consistent with those ascribed to the C=S=O group in related structures.[8,9]

Concurrent with the above reactions in the side chain, substitution reactions with nucleophiles occur at position 9 of the acridinium ring. Thus when **2** was treated with an excess of methylamine, the imine **3** was formed in 50% yield. In the case of dodecylamine, the 9-dodecylaminoacridinium chloride derivative **4** was obtained in 65% yield. The reaction of **2** with alcohols followed by brief exposure to water containing triethylamine during the isolation procedure generated the



carbonyl groups in position 9 of the acridine ring in all cases. Pyrolysis of **2** led to the loss of the side chain resulting in the known[10] 9-chloroacridine **5.**

The structure of **2** was unambiguously established from a crystal structure analysis. The conformation of a molecule of **2** is shown in Figure 1. The coordination about the sulfur atom is tetrahedral [the distances and angles about S are S–Cl, 2.331 (6); S–C, 1.668 (8); S–O, 1.462 (8) Å; Cl–S–C, 105.2 (3); Cl–S–O, 102.8 (4); C–S–O, 107.2 (4)°]. The S–Cl distance is substantially greater than the usual S–Cl distance of 2.01 Å[11] and the S–C distance is slightly shorter than that for S=C distances (1.71 ± 0.01[11]). Similar S–Cl distances [2.323 (3) and 2.259 (3) Å] were found in bis(*p*-chlorophenyl) sulfide[12] where the sulfur coordination is trigonal bipyramidal. The dihedral angle between the plane of the S–C–COCl moiety and the mean plane of the three fused rings is 77°. The three fused rings are not coplanar. The dihedral angle between the planes of the two $C_6$ rings of the fused ring system is 7.6°.

## Experimental Section

All melting points were taken in capillaries heated in oil baths, and are corrected. Infrared spectra were determined on a Digilab FTS14 or a Perkin-Elmer 621 spectrometer, mass spectra on a Varian MAT CH5 or a CEC-21-110 spectrometer, nuclear magnetic resonance spectra on a Jeolco C-60H, a Varian XL-100, or a Varian HA-100 spectrometer, using tetramethylsilane as internal standard, and ultraviolet spectra with a Cary 14M or 15 recording spectrometer. Solvents used were of reagent grade purity. Petroleum ether used boils at 30–60 °C. Unless otherwise specified, all solvents were evaporated on a Büchi Rotavapor evaporator under water-aspirator pressure using a water bath set at 30–80 °C.

**9-Chloroacridinium 2-Chloro-1-(chlorosulfinyl)-2-oxoethylide (2).** A mixture of 75.90 g (0.30 mol) of 9-oxo-10-acridanacetic acid (**1**), 350 ml of thionyl chloride, and 500 ml of 1,2-dimethoxyethane was heated to reflux for 2 h. On cooling the crimson red prisms of **2** were obtained. These were collected by filtration, washed with 1,2-dimethoxyethane followed by ether, and then dried in vacuo at 60 °C. They weighed 106.0 g (95%), mp 205–208 °C. These crystals were used for x-ray crystallographic analysis, spectral, and elemental analyses without recrystallization: ir (KBr) 1690 (s), 1603 (m), 1570 (m), 1530 (m), 1378 (m), 1335 (m), 1270 (m), 1122 (s), 937 (s), and 763 $cm^{-1}$ (s); uv max ($CH_3CN$) 208 nm (ε 20 200), 260 (39 500), 350 (sh, 6800), 365 (10 600), 388 (7850), and 430–480 (sh, 2100).

Anal. Calcd for $C_{15}H_8Cl_3NO_2S$: C, 48.35; H, 2.16; N, 3.76; Cl, 28.54; S, 8.60. Found: C, 48.60; H, 2.23; N, 3.65; Cl, 28.28; S, 8.78.

***N*-Methyl-9-(methylimino)-10-acridanacetamide (3).** A mixture of 7.40 g (20.0 mmol) of **2** and 0.380 mol of methylamine (100 ml of a 3.8 M solution in tetrahydrofuran) was stirred at room temperature for 1 h. To this was added 30 ml of water, and the mixture was evaporated. The residual oil was extracted into dichloromethane. The dichloromethane layer was dried ($Na_2SO_4$) and evaporated to dryness. The residue, on trituration with ether, afforded crude yellow amorphous solid which was recrystallized from ethanol to give 2.70 g (50%) of **3** as tan prisms: mp 234–236 °C; ir (KBr) 3280, 1660, 1626, and 1600 $cm^{-1}$; uv max (ethanol) 220 nm (ε 28 200), 245 (sh, 22 300), 257 (25 300), 268 (24 800) 285 (sh, 9700), 377 (7300), 410 (4200), and 430 (4000); NMR ($CDCl_3$) δ 2.75 (d, 3, $NHCH_3$), 3.69 (s, 3, $NCH_3$), and 4.58 ppm (s, 2, $CH_2$); mass spectrum *m/e* 279 ($M^+$).

Anal. Calcd for $C_{17}H_{17}N_3O$: C, 73.10; H, 6.13; N, 15.04. Found: C, 72.90; H, 6.13; N, 15.27.

**9-(Dodecylamino)-10-[(dodecylcarbamoyl)methyl]acridinium Chloride (4).** A mixture of 15.0 g (42.0 mmol) of **2**, 25.0 g (135 mmol) of dodecylamine, and 500 ml of tetrahydrofuran was stirred at room temperature for 2 h. After the addition of 50 ml of water, tetrahydrofuran was evaporated. The residual aqueous suspension was extracted with dichloromethane. The dichloromethane layer was dried ($Na_2SO_4$) and evaporated to dryness. The residue on trituation with ether afforded a solid which was recrystallized from methanol yielding 15.20 g (65%) of **4** as yellow needles: mp 174–176 °C; ir (KBr) 3200, 1685, and 1590 $cm^{-1}$; uv max (2-PrOH) 222 nm (ε 22 000), 260 (sh, 35 600), 271 (49 000), 290 (sh, 7000), 322 (sh, 2300), 417 (10 800), and 437 (10 600); mass spectrum *m/e* 587 ($M^+$ of free base).

Anal. Calcd for $C_{39}H_{62}ClN_3O$: C, 75.02; H, 10.00; N, 6.73; Cl, 5.68. Found: C, 74.86; H, 9.90; N, 6.62; Cl, 5.74.

**9-Chloroacridine (5).**[10] A mixture of 5.00 g (13.40 mmol) of **2** and 25 ml of mineral oil was heated to 210 °C till all gaseous evolution had ceased (0.5 h). On cooling, filtration and washing with petroleum ether afforded 3.0 g of 9-chloroacridinium chloride as a greenish-yellow solid, mp 244–247 °C. This material was sublimed at 180–200 °C in vacuo to afford 1.60 g of yellow-red prisms, mp 248–250 °C. An analytical sample was prepared by recrystallization from acetonitrile to afford yellow needles, mp 245–248 °C.

Anal. Calcd for $C_{13}H_9Cl_2N$: C, 61.10; H, 3.55; N, 5.48. Found: C, 61.43; H, 3.69; N, 5.56.

A mixture of 250 mg (1.0 mmol) of 9-chloroacridinium chloride, 10 ml of 2 N sodium hydroxide, and 10 ml of dichloromethane was stirred at room temperature for 5 min. The dichloromethane layer was dried ($Na_2SO_4$) and evaporated to dryness. The residue on crystallization from dichloromethane–petroleum ether afforded 110 mg of **5** as buff prisms, mp 118–120 °C (lit.[10] mp 119–120 °C).

**2-Hydroxyethyl 9-Oxo-10-acridanacetate (6a).** A mixture of 10.0 g (27.0 mmol) of **2** and 35 ml of ethylene glycol was stirred at room temperature for 16 h. This reaction mixture was poured into a mixture of 25 ml of triethylamine, 500 ml of dichloromethane, and 500 ml of water. The dichloromethane layer was dried ($Na_2SO_4$) and evaporated to dryness. The residue on crystallization from acetone–hexane afforded 3.50 g (45%) of **6a** as light cream needles, mp 169–172 °C. Recrystallization from acetone–hexane afforded cream needles: mp 175–178 °C; ir (KBr) 3430, 1730, 1630, and 1600 $cm^{-1}$; uv max (2-PrOH) 214 nm (ε 26 400), 253 (52 400), 290 (2600), 355 (sh, 3900), 374 (9000), and 394 (11 000); NMR ($CDCl_3$) δ 5.20 (s, 2, $NCH_2$); mass spectrum *m/e* 297 ($M^+$).

Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.08; N, 4.71. Found: C, 68.53; H, 5.05; N, 4.61.

**Dodecyl 9-Oxo-10-acridanacetate (6b).** A mixture of 10.0 g (27.0 mmol) of **2** and 35 ml of dodecanol was stirred at room temperature for 16 h. This mixture was then poured into a mixture of 25 ml of triethylamine, 500 ml of dichloromethane, and 500 ml of water. The dichloromethane layer was dried ($Na_2SO_4$) and evaporated to dryness. The residue on crystallization from petroleum ether afforded 8.50 g (75%) of **6b** as buff needles, mp 74–77 °C. Recrystallization from dichloromethane–petroleum ether afforded buff needles: mp 79–81 °C; ir (KBr) 1730, 1630, and 1600 $cm^{-1}$; uv max (2-PrOH) 214 nm (ε 22 650), 253 (49 950), 299 (2550), 358 (sh, 4400), 376 (8700), and 394 (10 500); NMR ($CDCl_3$) δ 5.04 (s, 2, $NCH_2$); mass spectrum *m/e* 421 ($M^+$).

Anal. Calcd for $C_{27}H_{35}NO_3$: C, 76.92; H, 8.36; N, 3.32. Found: C, 77.21; H, 8.35; N, 3.34.

**Methyl 9-Oxo-α-sulfinyl-10-acridanacetate (7).** A mixture of 37.20 g (10.0 mmol) of **2** and 500 ml of methanol was stirred at room temperature for 2 h. A clear red solution formed. On additional stirring, **7** precipitated as a pink, amorphous solid. This was collected by filtration, washed with methanol, and dried at 60 °C. It weighed 20.0 g (65%), mp 176–178 °C. On recrystallization from dichloromethane–petroleum ether, red prisms were obtained: mp 173–175 °C; ir (KBr) 1740, 1638, 1606, 1173, and 1085 $cm^{-1}$; uv max (2-PrOH) 214 nm (ε 20 900), 252 (42 400), 285 (sh, 6500), 365 (sh, 6500), 378 (7200), 395 (sh, 3100), and 455 (490); NMR showed no $CH_2$ signal; mass spectrum *m/e* 313 ($M^+$).

Anal. Calcd for $C_{16}H_{11}NO_4S$: C, 61.33; H, 3.53; N, 4.47; S, 10.23. Found: C, 61.55; H, 3.57; N, 4.57; S, 10.09.

**Methyl 9-Oxo-10-acridanacetate (8).** A mixture of 10.0 g (32.0 mmol) of **7**, 10 ml (71.0 mmol) of triethylamine, 300 ml of dichloromethane, and 300 ml of water was stirred at room temperature for 0.5 h. The dichloromethane layer was separated, dried ($Na_2SO_4$), and evaporated to dryness. The residue on crystallization from dichloromethane–petroleum ether afforded 4.70 g (55%) of **8** as colorless needles, mp 207–209 °C. The melting point was unchanged on recrystallization from the same solvents: ir (KBr) 1740, 1630, and 1600 $cm^{-1}$; uv spectrum (2-PrOH) essentially the same as those of **6a** and **6b**; NMR ($CDCl_3$) δ 5.05 (s, 2, $NCH_2$); mass spectrum *m/e* 267 ($M^+$).

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.71; H, 4.88; N, 5.14.

**Crystallography.** Crystals of **2** ($C_{15}H_8Cl_3NO_2S$, mol wt 372.66) are monoclinic, space group $P2_1/c$, with $a$ = 8.620 (9), $b$ = 11.942 (18), $c$ = 14.958 (12) Å, β = 103.03 (5)°, and $d_{calcd}$ = 1.649 g $cm^{-3}$ for $Z$ = 4.

The intensity data were measured on a Hilger-Watts diffractometer (Ni filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). The size of the crystal used for data collection was approximately 0.08 × 0.2 × 0.5 mm. A total of 2400 independent reflections (θ <57°) were measured, of which 1409 had intensities which were significantly greater than background [$I > 2.5\sigma(I)$]. The data were corrected for absorption (μ = 68.3 $cm^{-1}$). The structure was solved by a multiple solution procedure[13] and was refined by full-matrix least squares. The

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 $\pm 0.2$ 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 $\delta$ 2.35 ppm. Slow disappearance of this signal and simultaneous appearance of