the amine salt. This salt was treated with NaOH to give 9.42 g (76%) of β-durylethyldimethylamine (**18**): bp 93° (0.26 mm) (solidified on cooling in an ice bath); $n^{25}D$ 1.5165; ir (neat, strong peak) 3000–2700, 1460, 1045, 1035, 1015, 864, and 857 cm^{-1}; nmr 6.82 (s, 0.8 H, aromatic) and 3.18–2.10 (m, 22.0 H, others).

Anal. Calcd for $C_{14}H_{23}N$: C, 81.89; H, 11.29; N, 6.82. Found: C, 81.82; H, 11.05; N, 6.90.

Methylation of 4.30 g (0.02 mol) of this amine was effected with 5.70 g (0.04 mol) of methyl iodide in acetonitrile to give 7.14 g (98%) of methiodide **19**, mp 282–285° dec.

Anal. Calcd for $C_{15}H_{26}NI$: C, 51.87; H, 7.55; N, 4.03. Found: C, 52.11; H, 7.44; N, 4.06.

β elimination was effected by adding 5.90 g (0.017 mol) of this methiodide **19** to 0.02 mol of KNH_2 in 150 ml of liquid ammonia[5,6] to give 2.11 g (78%) of 2,3,5,6-tetramethylstyrene (**20**): bp 51–52° (0.12–0.15 mm); mp 34.5–35.5°; ir (neat) 3080 (C=CH_2), 1625 and 1600 (C=C), and 866 cm^{-1} (pentasubstituted benzene ring); nmr 6.89 (s, C_4-H) and 6.74 (X portion of ABX pattern, vinyl αH, 2.1 H), 5.31 (center of AB portion of ABX pattern, J_{gem} = 2.4 Hz, vinyl βH), and 2.20 ppm (d, 12.0 H, C_2-CH_3, C_3-CH_3, C_5-CH_3 and C_6-CH_3).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.88; H, 10.02.

Conversion of *exo*-Methylene Bicyclic Amine 14 into Methiodide 27. Treatment with Sodium Amide.—Methylation of 3.92 g (0.0179 mol) of this amine was effected with 5.10 g (0.0358 mol) of methyl iodide in dry acetone (stirred for 3.5 hr) to give 2.10 g (33%) of methiodide **27** (white powder): mp 224–226° dec; ir (KBr) 3010 (C=CH_2), 3070 (cyclopropyl methylene), 1810 (C-H), 1635, 1600 and 1575 cm^{-1} (C=C).

Anal. Calcd for $C_{16}H_{28}NI$: N, 3.88. Found: N, 3.56.

To a stirred suspension of 0.0175 mol of $NaNH_2$ in 70 ml of liquid ammonia[5,6] was added 2.10 g (0.0058 mol) of methiodide **27**. After 3 hr, the deep orange-red mixture was decomposed with NH_4Cl, and the liquid ammonia was replaced by 50 ml of anhydrous ether.[7] The resulting mixture was worked up, but no isolable product was obtained in appreciable amount.

Registry No.—Sodium amide, 12125-45-0; **2**, 19990-87-5; **3**, 19990-88-6; **4**, 6968-88-3; β-isodurylethyldimethylamine, 5336-63-0; **5**, 19990-91-1; **9**, 19990-92-2; **10**, 19990-93-3; **11**, 19990-94-4; **12**, 19990-95-5; **13**, 19990-96-6; **14**, 19990-97-7; **18**, 19990-98-8; **19**, 19990-99-9; **20**, 2039-91-0; **21**, 19991-01-6; **22**, 19991-02-7; **23**, 3937-22-2; β-hydroxyethyldurene, 19991-04-9; β-bromoethyldurene, 19991-05-0; **27**, 19991-06-1.

Aminolyses of Sulfinic Acid Derivatives[1]

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A series of alkane- and arenesulfinamides was prepared from the corresponding sulfinyl chloride. Treatment of the chlorolysis product of dithiodiglycolic acid with morpholine produced 4-morpholinosulfinylacetomorpholide (**1**). Dimorpholide **1** was a stable, water-soluble, and slightly acidic substance. The infrared spectrum resembled that of the simple alkanesulfinamides in the region of 1500–650 cm^{-1}. However, between 3000 and 2500 cm^{-1} the spectrum exhibited a series of bands characteristic of amine salts. In addition, there were two strong bands at 1630 and 1610 cm^{-1} assignable to conjugated C=C stretching and C=O stretching vibrations. The ultraviolet spectrum of **1** exhibited one maximum at 273 mμ (ε 14,000) which did not shift in the presence of base. From a consideration of the spectral data and the saltlike physical properties of compound **1**, it appears that its structure is best represented by the betaine resonance hybrid **1a** ↔ **1b**. Under controlled conditions, oxidation of 3,3′-dithiodipropionic acid by chlorine led to 1,2-oxathiolan-5-one 2-oxide (**3**), which upon aminolysis with aromatic amines gave sulfonyl dipropionamides **5**. The structure of **3** was confirmed by molecular weight determinations (Rast method), saponification equivalent, alkaline permanganate oxidation, and elementary analysis. Mechanisms for the formation of **3** and its aminolysis products are presented.

In a search for agents capable of reconstituting reduced keratin, a process involving mild oxidation of thiol to disulfide groups, our attention turned to the little known class of sulfinamides $RSONR^1R^2$. Several years ago, Smith and Grasley[3] reported, as part of their work relating to antiradiation drugs, the oxidation of 2-aminoethanethiol to its disulfide in the presence of certain arenesulfinamides.

$$RSONR_2 + 2R'SH \longrightarrow R'SSR' + RSNR_2 + H_2O$$

While arenesulfinamides have been known for some time,[4] amides derived from alkanesulfinic acids became accessible only after a facile method for the synthesis of alkanesulfinyl chlorides had been discovered.[5] Douglass and Farah[6] reported the aminolysis of methanesulfinyl chloride with several aromatic amines, and Moriarty[7] more recently applied this method to the synthesis of a few N,N-dialkylalkanesulfinamides, the first members of this class of compounds.[8]

The sulfinamides prepared in our laboratories by amonolysis and aminolysis of a variety of arene- and alkanesulfinyl chlorides are listed in Table I. In general, the sulfinamides obtained were unpleasant smelling, colorless liquids, distillable at low pressures. They were soluble in most organic solvents; the lower molecular weight derivatives and those containing morpholine groups were unstable and discolorized gradually on exposure to air. The sulfinamides were rapidly oxidized by alkaline permanganate, but the corresponding sulfonamides expected as end products of the oxidation[6] could not be isolated. The infrared (ir) spectra of the sulfinamides showed strong absorptions at 1070 and 1010 cm^{-1} assignable to S=O stretching vibrations.[9]

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

(2) Ethicon, Inc., Somerville, N. J.

(3) W. T. Smith, Jr. and M. Grasley, Abstract, the 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962, p 36N.

(4) L. C. Raidord and S. E. Hazlet, *J. Amer. Chem. Soc.*, **57**, 2172 (1935).

(5) (a) I. B. Douglass and D. R. Poole, *J. Org. Chem.*, **22**, 536 (1957); (b) I. B. Douglass and B. S. Farah, *ibid.*, **23**, 330 (1958); (c) I. B. Douglass, B. S. Farah, and E. G. Thomas, *ibid.*, **26**, 1996 (1961); (d) I. B. Douglass and B. S. Farah, *Org. Syn.*, **40**, 62 (1960).

(6) I. B. Douglass and B. S. Farah, *J. Org. Chem.*, **23**, 805 (1958).

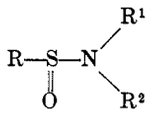
(7) R. M. Moriarty, *Tetrahedron Lett.*, No. 10509 (1964).

(8) The use of a number of N,N-dialkylsulfinamides as bird repellants without claiming or describing a method of preparation has been disclosed: L. D. Goodhue, R. P. Louthan, and K. E. Cantrel, U. S. Patent 2,955,980 (1960).

(9) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958, pp 350–364.

TABLE I

SULFINAMIDES



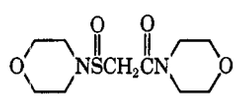
R	R¹	R²	% yield[a]	Bp (mm), °C	Empirical formula	Registry no.	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % S	Found, % C	Found, % H	Found, % N	Found, % S
CH_3	CH_3	CH_3	16	38 (1.2)	[b]	920-56-9								
CH_3	C_2H_5	C_2H_5	11	55 (1.8)	$C_5H_{13}NOS$	921-77-7	45.39	9.69	10.36	23.72	44.21	10.00	10.31	23.80
CH_3	$CH_2CH_2OCH_2CH_2$		42	81 (0.25)	$C_5H_{11}NO_2S$	13455-93-1	40.24	7.43	9.39	21.49	40.53	7.52	9.39	21.23
CH_3	H_3C CH_3 | | $CH_2CHOCHCH_2$		17	72 (0.1)	$C_7H_{15}NO_2S$	19955-33-0	47.42	8.53	7.90	18.09	47.68	8.50	7.70	17.94
CH_3	CH_3 | $CH_2CH_2NCH_2CH_2$		40	68 (0.08)	$C_6H_{14}N_2OS$	19955-34-1	44.41	8.70	17.27	19.77	44.43	8.66	16.88	193.5
C_2H_5	CH_3	CH_3	13	50 (4)	[b]	921-05-1								
C_2H_5	C_2H_5	C_2H_5	39	55 (1.3)	$C_6H_{15}NOS$	10408-13-6	48.28	10.13	9.39	21.49	48.25	10.34	9.20	21.18
C_2H_5	$CH_2CH_2OCH_2CH_2$		27	84 (0.1)	$C_6H_{13}NO_2S$	19955-37-4	44.14	8.03	8.58	19.65	44.37	8.38	8.40	19.30
$CH_3CH_2CH_2$	CH_3	CH_3	20	55 (1.1)	$C_5H_{13}NOS$	923-05-7	44.41	9.69	10.36	23.72	44.64	10.06	10.65	23.52
$CH_3CH_2CH_2$	C_2H_5	C_2H_5	73	60 (0.25)	$C_7H_{17}NOS$	19955-39-6	51.49	10.50	8.58	19.64	51.04	10.56	8.70	19.80
$CH_3CH_2CH_2$	$CH_2CH_2OCH_2CH_2$		80	88 (0.08)	$C_7H_{15}NO_2S$	19955-40-9	47.42	8.53	7.90	18.09	47.45	8.77	8.10	18.33
$(CH_3)_2CH$	H	H	9	64–65[c]	C_3H_9NOS	1955-41-0	33.62	8.46	13.07	29.29	33.62	8.70	13.10	29.71
$(CH_3)_2CH$	CH_3	CH_3	41	66 (6)	$C_6H_{13}NOS$	921-15-3	44.41	9.69	10.36	23.72	44.33	9.77	10.47	23.61
$(CH_3)_2CH$	C_2H_5	C_2H_5	50	60 (0.4)	$C_7H_{17}NOS$	19955-43-2	51.49	10.50	8.58	19.63	51.26	10.43	8.72	19.92
$(CH_3)_2CH$	$CH_2CH_2OCH_2CH_2$		38	80 (0.1)	$C_7H_{15}NO_2S$	19955-44-3	47.42	8.53	7.90	18.09	47.05	8.77	8.00	18.15
C_6H_5	CH_3	CH_3	43	73 (0.1)	$C_8H_{11}NOS$	5539-54-8	56.77	6.55	8.28	18.95	56.67	6.68	8.39	18.88
p-$NO_2C_6H_4$	$CH_2CH_2OCH_2CH_2$		19	128–130[d]	$C_{10}H_{12}N_2O_4S$	19955-46-5	46.86	4.72	10.93	12.51	47.10	4.60	11.08	12.36

[a] Yield is based on sulfinyl chloride. [b] R. M. Moriarty, *J. Org. Chem.*, **30**, 600 (1965). [c] Melting point; compound was recrystallized from ether. [d] Melting point; compound was recrystallized from an ethanol–methanol mixture.

In the primary amide, 2-propanesulfinamide, absorption occurred at 1040 and 1010 cm^{-1}, a shift indicative of hydrogen bonding;[10] strong association also was evident from the greatly shifted N—H stretching absorption at 3200 and 3100 cm^{-1}. In addition, the sulfinamides absorbed in the region of 700–660 cm^{-1} (C—S stretching[9] at 920–900 cm^{-1} [11]).

The oxidative power of the sulfinamides toward mercapto groups was determined semiempirically on ammonium and monoethanolamine thioglycolate reduced hair by the waving efficiency test of Kirby.[12] Of all of the compounds tested, only 2-propanesulfinamide showed promising oxidative properties. Since many of the compounds were not sufficiently soluble under the aqueous testing conditions, the incorporation of a solubilizing moiety became desirable and to this end the synthesis of a carboxyalkanesulfinamide was attempted.

Chlorination of dithiodiglycolic acid in the presence or absence of acetic acid followed by aminolysis with morpholine yielded the dimorpholide **1** instead of the desired carboxymethylsulfinamide.

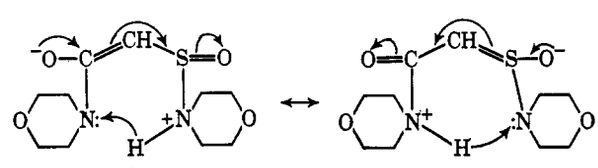


1

This finding was not unexpected in view of the report of Douglass and Farah[13] who isolated analogous diamides when they subjected 3-mercaptopropionic acid and 4,4′-dithiodibutyric acid to chlorolysis and subsequently treated the resulting intermediate with aniline.

The dimorpholide **1**, mp 189–190°, was a stable, water-soluble, and slightly acidic substance (pH 5.7 for a 1% aqueous solution). The compound readily decolorized bromine and alkaline permanganate but was not affected by treatment with neutral hydrogen peroxide. The ir spectrum resembled that of the simple alkanesulfinamides in the region of 1500–650 cm^{-1}. However, between 3000 and 2500 cm^{-1} the spectrum exhibited a series of bands characteristic of amine salts. In addition, there were two strong bands at 1630 and 1610 cm^{-1} assignable to conjugated C=C stretching and C=O stretching vibrations. The ultraviolet (uv) spectrum of **1** exhibited one maximum at 273 mμ (ϵ 14,000) which did not shift in the presence of base. The high absorbance at this wavelength is strongly reminiscent of the spectrum of the predominantly enolic acetylacetone [273 mμ (ϵ 10,000)].[14]

From a consideration of the spectral data and the saltlike physical properties of compound **1**, it appears that its structure is best represented by the betaine resonance hybrid **1a** ↔ **1b**; abstraction of a proton by base, it may be noted, does not alter the character of the chromophore in this representation.



1a **1b**

Attempts to extend the aminolysis of chlorosulfinylacetyl chloride to amines other than morpholine were unsuccessful. A variety of alkyl, aryl, and heterocyclic amines (including piperidine) were employed, but in every instance the reaction products consisted of dark oils or tars which could not be purified. The unique success achieved with morpholine can be rationalized on the basis of its high nucleophilic character which is

(10) E. D. Amstutz, I. M. Hunsberger, and J. J. Chessik, *J. Amer. Chem. Soc.*, **73**, 1220 (1951).

(11) The absorption around 900 cm^{-1} appears to be specific for sulfinamides since other tetravalent sulfur derivatives (sulfinic acids, sulfoxides, etc.) do not exhibit peaks in this region.

(12) D. H. Kirby, *Drug Cosmetic Ind.*, **80**, 314 (1957).

(13) I. B. Douglass and B. S. Farah, *J. Org. Chem.*, **26**, 351 (1961).

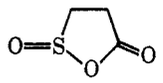
(14) M. J. Kamlet, "Organic Electronic Spectral Data," Vol. 1, Interscience Publishers, New York, N. Y., 1960, pp 60, 61.

coupled with a low basicity.[15] This combination of properties greatly favors bimolecular substitution over elimination reactions.[16] In the presence of more basic amines, however, the elimination reaction predominates which in the case of the postulated intermediate sulfinylacetyl chloride may give rise to a highly labile sulfine.[17]

Since the ability of the dimorpholide **1** to reconstitute disulfide bonds in reduced-hair keratin was equal to that of hydrogen peroxide,[12] it seemed desirable to examine similar diamides in the homologous series.

Chlorolysis of 3,3′-dithiodipropionic acid with 3 mol of chlorine, followed by reaction with *n*-butylamine gave the expected dibutyramide derivative, *n*-$C_4H_9NHC(=O)CH_2CH_2S(=O)NHC_4H_9$-*n* (**2**).

During the chlorination step the formation of a precipitate was observed. When the reaction was terminated after a chlorine uptake of only 2 mol, the solid product could be obtained in its maximum yield. The material contained no chlorine, and elementary analysis, molecular weight determinations (Rast method), saponification equivalent, and alkaline permanganate oxidation according to the method of Allen[18] indicated that the hitherto-unknown anhydride of β-carboxyethanesulfinic acid, 1,2-oxathiolan-5-one 2-oxide (**3**), was at hand.



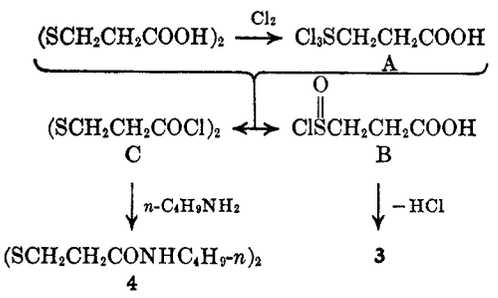
3

Compound **3** was insoluble in cold water, but it could be recrystallized from hot neutral or acidic aqueous solutions; it dissolved readily in base, and it could be recovered unchanged upon neutralization of its basic solution. The material could not be oxidized by hydrogen peroxide to the known 1,2-oxathiolan-5-one 2,2-dioxide.[19] The ir spectrum of **3** showed major bands at 1700 (C=O stretching), 1320 and 1240 (cyclic C—O stretching), and 1150 and 1110 cm^{-1} (S=O stretching).

The nmr spectrum of **3** had signals at τ 7.0 (d, 2 H), 6.6 (m, 1 H), and 6.1 (m, 1 H). Since chemically there are only two species of protons in **3**, the nonequivalence of one of the species is required by the spectrum. The chemical shift at τ 7.0, a doublet of doublets, can readily be assigned by analogy with succinic anhydride[20] to the protons adjacent to the carbonyl group. The nonequivalence of the geminal protons adjacent to the sulfinyl group is a further demonstration of tetravalent sulfur asymmetry.[21]

In addition to **3**, chlorolysis of 3,3-dithiodipropionic acid with 2 mol of chlorine gave rise to an oil which could not be distilled without decomposition. Reaction of the crude oil with butylamine resulted in the formation of N,N′-dibutyldithiodipropionamide (**4**), a compound obviously derived from dithiodipropionyl chloride. The formation of this acid chloride as by-product in the synthesis of **3** suggests the reaction mechanism shown in Scheme I.

SCHEME I



In this reaction sequence the starting material disproportionates in the presence of its primary chlorination product (A) according to the general scheme of Douglass, *et al.*,[5c] to yield compounds B and C. The stoichiometry of this reaction requires only 1.5 mol of chlorine/mol of starting material.

$$2(SCH_2CH_2COOH)_2 + 3Cl_2 \longrightarrow C + 2B + 2HCl$$

In passing it may be noted that the nature of the products isolated from the chlorolysis of 3,3-dithiodipropionic acid, with less than 3 mol of chlorine, favors an intermolecular solvolysis of intermediate A[22] rather than the intramolecular mechanism proposed by Douglass and Farah.[13]

Aminolysis of 1,2-oxathiolan-5-one 2-oxide (**3**) with aliphatic amines led to complex products which could not be identified, but the reaction with aniline and substituted anilines gave moderate yields of the symmetrical sulfones **5**. The structure of the unsubstituted dianilide **5** (Ar = C_6H_5) was proven by comparison with an authentic sample prepared from 3,3′-sulfonyldipropionic acid *via* the acid chloride. The unexpected formation of the sulfones by aminolysis of **3** can be rationalized tentatively as shown in Scheme II.

This scheme postulates—in analogy with the observation of Kharasch, *et al.*,[19] on the aminolysis of 1,2-oxathiolan-5-one 2,2-dioxide—a nucleophilic attack at C-5 resulting in the sulfinic acid intermediate D. Compounds of this type are known to be subject to facile base-catalyzed β eliminations involving expulsion

(15) H. K. Hall, Jr., *J. Amer. Chem. Soc.*, **78**, 2570 (1956).
(16) N. H. Cromwell and P. H. Hess, *ibid.*, **83**, 1237 (1961).
(17) W. A. Sheppard and J. Diekmann, *ibid.*, **86**, 1891 (1964).
(18) P. Allen, Jr., *J. Org. Chem.*, **7**, 23 (1942).
(19) M. S. Kharasch, T. H. Chao, and H. C. Brown, *J. Amer. Chem. Soc.*, **62**, 2393 (1940).
(20) N. S. Bhacca, B. P. Hollis, L. F. Johnson, and E. A. Pier, "N.M.R. Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963.
(21) (a) G. M. Whitesides, D. Holz, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 2628 (1964); (b) J. G. Pritchard and P. C. Lauterbur, *ibid.*, **83**, 2105 (1961); (c) K. Mislow, A. L. Ternay, Jr., and J. T. Meillilo, *ibid.*, **85**, 2329 (1963); (d) R. M. Moriarty, *J. Org. Chem.*, **30**, 600 (1965).

(22) The formation of the ultimate reaction product, 3-chlorosulfinylpropionyl chloride, which arises when chlorine is used in excess (3 mol) may be explained by the following scheme.

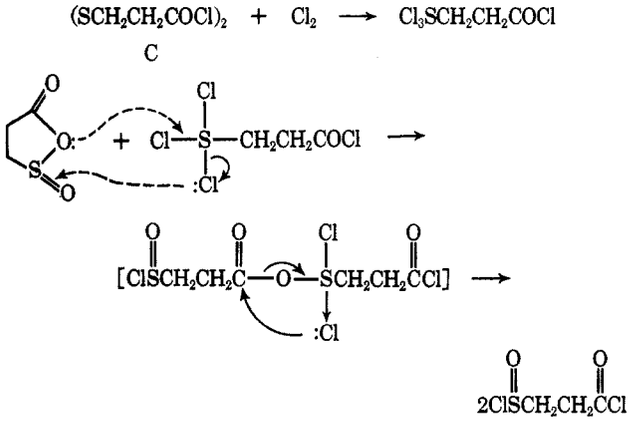
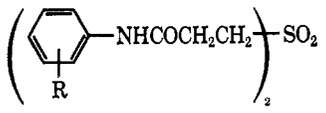
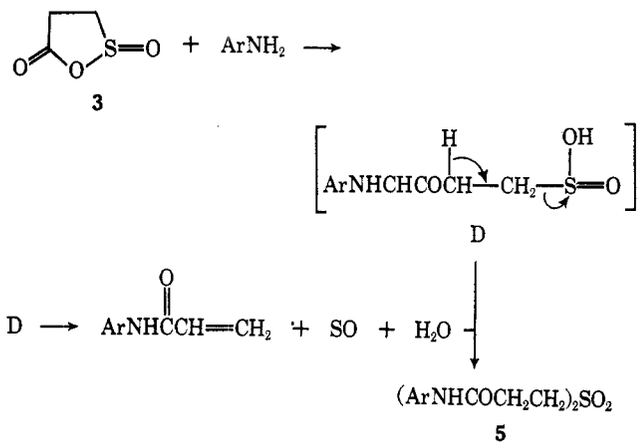


TABLE II
SULFONES



R	% yield	Mp, °C	Recrystn solvent	Empirical formula	Registry no.	Calcd, % C	H	N	S	Cl	Found, % C	H	N	S	Cl
H	8	246–247	EtOH	$C_{18}H_{20}N_2O_4S$	19955-47-6	59.98	5.59	7.77	8.90		59.82	5.55	7.75	8.97	
o-CH_3	12	255	EtOH	$C_{20}H_{24}N_2O_4S$	19955-48-7	61.83	6.23	7.21	8.26		61.95	6.45	7.14	7.83	
p-CH_3	20	271–272	EtOH	$C_{20}H_{24}N_2O_4S$	19955-49-8	61.83	6.23	7.21	8.26		61.65	6.25	7.33	8.15	
o-Cl	21	234–235	EtOH	$C_{18}H_{18}Cl_2N_2O_4S$	19955-50-1	50.35	4.23	6.53	7.47	16.52	50.55	4.36	6.53	7.35	16.42
p-Cl	6	290–291	Acetone–EtOH (2:3)	$C_{18}H_{18}Cl_2N_2O_4S$	19955-51-2	50.35	4.23	6.53	7.47	16.52	50.28	4.45	6.56	7.60	16.68
o-OCH_3	2	175–176	Acetone–hexane (1:3)	$C_{20}H_{24}N_2O_6S$	19955-52-3	57.13	5.75	6.66	7.63		57.24	5.78	6.87	7.75	

SCHEME II



of a sulfur fragment.[23] Combination of D with its β-elimination product (acrylanilide) then can be expected to lead to **5** in accordance with the well-known synthesis of sulfones by the addition of sulfinic acids to α,β-unsaturated species.[24]

Experimental Section[25]

Preparation of Sulfinamides. General Procedure.—To a stirred solution of 0.4 mol of an amine in 150 ml of methylene chloride, 0.2 mol of a sulfinyl chloride[6c,26] was added dropwise over a period of 1 hr. The reaction was run under a nitrogen atmosphere and at a temperature of −20 to −40° maintained by means of an acetone–Dry Ice bath. After complete addition, the reaction mixture was stirred for 1 hr at room temperature. The precipitate consisting of amine hydrochloride was filtered off and the solvent was removed from the filtrate by distillation. The reaction residue, in the case of a solid, was recrystallized from an appropriate solvent; liquid sulfinamides were distilled at reduced pressure and at temperatures not exceeding 90°. At higher distillation temperatures extensive decomposition took place.

The individual sulfinamides prepared by the above method are listed in Table I. The ir spectrum gave signals at 1070–1010 (S=O) and 700–660 cm^{-1} (C—S).

4-Morpholinosulfinylacetomorpholide (**1**).—To a stirred suspension of 45.5 g (0.25 mol) of dithiodiglycolic acid in 200 ml of methylene chloride was added over a period of 1 hr 36.0 g (0.5 mol) of chlorine gas while the reaction temperature was maintained at 0–10° by means of an acetone–Dry Ice bath. Gradually all suspended material went into solution. After completed addition, the solution was stirred at room temperature and subsequently at 40° to remove all of the hydrogen chloride formed in the reaction. The solvent was removed under reduced pressure to leave an oily residue of crude chlorosulfinylacetyl chloride which was used as such in the following step.

A solution of 174 g (2.0 mol) of morpholine in 300 ml of methylene chloride was allowed to react with a solution of 80.5 g (0.5 mol) of the above crude chlorosulfinylacetyl chloride in 250 ml of methylene chloride according to the general procedure for the preparation of sulfinamides. After complete reaction, the solution was condensed to a volume of 250 ml. The solid, consisting mainly of morpholine hydrochloride, was filtered off and the filtrate was condensed further to a volume of 50 ml. The resulting precipitate was collected by filtration and recrystallized several times from 95% ethanol: yield 57 g (54%), mp 189–190°.

Anal. Calcd for $C_{10}H_{18}N_2O_4S$: C, 45.78; H, 6.91; N, 10.68 S, 12.23. Found: C, 45.68; H, 7.07; N, 10.55; S, 12.45.

Reactions of the chlorosulfinylacetyl chloride with aniline, piperidine, diethylamine, and N-methyl piperazine failed to give identifiable products.

N-*n*-Butyl-3-*n*-butylaminosulfinylpropionamide (**2**).—A solution containing 73 g (1 mol) of *n*-butylamine in 250 ml of methylene chloride was treated with a solution of 40 g (0.23 mol) of crude 3-chlorosulfinylpropionyl chloride[13] in 250 ml of methylene chloride according to the general procedure for the preparation of sulfinamides. After removal of the reaction solvent the semisolid residue was triturated with 100 ml of ethyl acetate and the solid consisting of *n*-butylamine hydrochloride was filtered off. The filtrate was washed several times with water and dried. After removal of the solvent there remained a colorless solid which was recrystallized from ethyl acetate: yield 13 g (20%), mp 83–84°.

Anal. Calcd for $C_{11}H_{24}N_2O_2S$: C, 53.19; H, 9.74; N, 11.28; S, 12.91. Found: C, 53.09; H, 9.73; N, 11.36; S, 12.98.

1,2-Oxathiolan-5-one 2-Oxide (**3**).—To a stirred solution containing 105 g (0.5 mol) of dithiodipropionic acid in 200 ml of methylene chloride was added 71 g (1.0 mol) of chlorine gas over a period of 2 hr. The reaction temperature was maintained at −20 to −40° and, after complete addition, the reaction mixture was allowed to warm to room temperature. The solution was filtered and the filtrate was worked up as described below. The precipitate was recrystallized several times from ethyl acetate: yield 28.5 g (48%), mp 148–150°.

Anal. Calcd for $C_3H_4O_3S$: C, 29.99; H, 3.36; S, 26.70; mol wt, 120. Found: C, 30.02; H, 3.57; S, 26.73; mol wt (Rast), 120.

N,N'-Dibutyldithiodipropionamide (**4**).—The filtrate from the preceding reaction was condensed under reduced pressure to leave an oily residue which was dissolved in 100 ml of methylene chloride. This solution was used for the acylation of 73 g (1 mol) of *n*-butylamine according to the conditions described for the preparation of compound **2**. After complete reaction, the reaction mixture was washed several times with water and dried. The solvent was removed under reduced pressure. The residue, a colorless solid, was recrystallized from ethyl acetate: yield 3.3 g (2%), mp 130–131°.

Anal. Calcd for $C_{14}H_{28}N_2O_2S_2$: C, 52.46; H, 8.80; N, 8.74; S, 20.01. Found: C, 52.33; H, 8.61, N, 8.53; S, 20.48.

(23) (a) A. T. Kader and C. J. M. Stirling, *J. Chem. Soc.*, 3686 (1962); (b) D. S. Campbell and C. J. M. Stirling, *ibid.*, 5869 (1964); (c) F. Weygand and W. Steglich, *Chem. Ber.*, **98**, 487 (1965); (d) T. J. Wallace, H. Pobiner, J. E. Hofmann, and A. Schriesheim, *J. Chem. Soc.*, 1271 (1965).

(24) E. Schjanberg, *Ber.*, **76**, 287 (1943).

(25) All melting points were measured in a Thomas–Hoover apparatus. Melting and boiling points are uncorrected. Ir curves were obtained on a Perkin-Elmer Model 21 and nmr measurements were made on a Varian A-60.

(26) I. B. Douglass, K. R. Brewer, and F. T. Martin, *J. Amer. Chem. Soc.*, **74**, 5770 (1952).

Aminolysis of 3. Preparation of Sulfones 5.—A mixture of 0.03 mol of **3** and 0.15 mol of an arylamine was heated for 12 hr under a nitrogen atmosphere at 130–160°. The reaction product was washed with consecutive portions of 10% hydrochloric acid and water. The washed material was dissolved in 100 ml of 95% ethanol; the solution was charcoaled and condensed to one-half volume. The product was filtered off and recrystallized from an appropriate solvent.

The individual sulfones prepared by this method are listed in Table II.

3,3′-Sulfonyldipropionanilide (5, Ar = C_6H_5).—A solution consisting of 9.9 g (0.05 mol) of 3,3′-sulfonyldipropionic acid,[27] 75 ml of thionyl chloride, and 100 ml of chloroform was refluxed for 48 hr. The solvent and excess thionyl chloride were removed by distillation and the residue was dissolved in 150 ml of methylene chloride. This solution was added dropwise to a stirred solution of 18.6 g (0.2 mol) of aniline in 150 ml of methylene chloride. Stirring at room temperature was continued for 2 hr after complete addition. The solid was filtered off and extracted several times with hot water. The water-insoluble material was recrystallized from ethanol: yield 7.4 g (41%), mp 246–247°.

The reaction product was identical (melting point, mixture melting point, and ir spectrum) with the material obtained from the aminolysis of 1,2-oxathiolan-5-one 2-oxide **3** with aniline.

(27) H. S. Schultz, H. B. Freyermuth, and S. R. Buc, *J. Org. Chem.*, **28**, 1140 (1963).

Registry No.—**1**, 10408-21-6; **2**, 19955-27-2; **3**, 19955-28-3; **4**, 927-42-4.

Preparation and Reactions of Diazo Ketones. V.[1] Normal and Abnormal Products from Thermal Wolff Rearrangement of 9-Phenylfluorene-9-carbonyldiazomethane

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As one test of the role of steric factors in leading to abnormal thermal Wolff rearrangement of the diazomethyl ketone **1** from triphenylacetic acid, diazomethyl ketone **5** was prepared from 9-phenylfluorene-9-carboxylic acid (**4a**). Thermal Wolff rearrangement of **5** in 1-hexanol and N-ethylmorpholine gave 50–55% of normal product **6** as well as 35–40% of abnormal product **7**. Decarboxylation of acid **7a** gave 1-methyl-9-phenylfluorene (**9**), which was synthesized from 1-methyl-9-fluorenone (**11**). Nmr spectra for these compounds provide confirmatory proof of structures. The formation of considerable normal product **6** in the 9-phenylfluorene example **5**, compared with none in the triphenylmethane case **1**, supports the view that steric factors are important in impeding normal rearrangement of the latter.

Some years ago in this laboratory, as a result of our interest in using the Arndt–Eistert synthesis of homologous acids in certain synthetic sequences, we undertook a series of investigations aimed at widening the scope of the method, improving the reliability of the experimental procedures, and throwing further light on the mechanisms of the reactions. Wilds and Meader[1a] reported solutions for two of the problems involved, the first concerning the preparation of diazo ketones from acid chlorides and higher diazohydrocarbons,[2,3] and the second an improved and more general method for rearranging diazo ketones to derivatives of the homologous acids.

With these problems clarified, we turned to a study of the synthetic and mechanistic consequences of increasing the steric requirement of the acid chloride on the formation of the diazo ketone, and also on the Wolff rearrangement of the latter. It was known that mesitoyl chloride failed to give a diazo ketone with diazomethane.[4,5] This diazo ketone prepared in another way, however, underwent normal rearrangement to the higher acid, as did 2,4,6-triisopropylbenzoyldiazomethane.[6] Consequently it is clear that the steric requirements of the two steps in the Arndt–Eistert sequence are quite different.

Significant results were obtained by Van Den Berghe[5] in the series *n*-butyryl, isobutyryl, and trimethylacetyl chloride with diazomethane and diazoethane, reflecting the increasing steric requirements, two aspects of which of which should be mentioned here. Reaction of trimethylacetyl chloride and diazomethane proceeded slowly but normally, under the proper conditions, to the diazo ketone (70% yield). With certain diazomethane solutions, however, trace impurities that had little or no effect with *n*- or isobutyryl chloride altered the course of reaction with trimethylacetyl chloride, giving chloromethyl *t*-butyl ketone (50–60% yield), even with an excess of diazomethane present.[7–9] Reaction of *diazoethane* with trimethylacetyl chloride gave several abnormal products instead of the diazo ketone, the latter being present at most only in small amounts.[5]

For rearrangement of these and other potentially sterically hindered diazo ketones, it was essential to

(1) For convenience in reference, we are now assigning to our earlier papers in the series Preparation and Reactions of Diazo Ketones the following numbers: (a) I, A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948); (b) II, C. E. Blades and A. L. Wilds, *ibid.*, **21**, 1013 (1956); (c) III, A. L. Wilds, J. Van Den Berghe, C. H. Winestock, R. L. von Trebra, and N. F. Woolsey, *J. Amer. Chem. Soc.*, **84**, 1503 (1962); (d) IV, A. L. Wilds, N. F. Woolsey, J. Van Den Berghe, and C. H. Winestock, *Tetrahedron Lett.*, 4841 (1965).

(2) (a) Because of the higher reactivity of diazoethane (*vs.* diazomethane), it was found that lower temperatures (−20°) and limited amounts of diazohydrocarbon were necessary to avoid further reaction of the diazo ketone and diazoethane with loss of N_2 to form a mixed azine.[1a,2b,c,3] (b) A. L. Meader, Jr., Ph.D. Thesis, University of Wisconsin, 1947. (c) G. Baddeley, G. Holt, and J. Kenner, *Nature*, **163**, 766 (1949).

(3) P. Yates, D. G. Farnum, and D. W. Wiley, *Chem. Ind.* (London), 69 (1958).

(4) (a) W. E. Bachmann and J. C. Sheehan, unpublished work cited by W. E. Bachmann and W. S. Struve, *Org. Reactions*, **1**, 38 (1942). (b) This failure of mesitoyl chloride to react was confirmed by Van Den Berghe with diazomethane and diazoethane, 90–98% of the acid chloride being recovered. For details see ref 5.

(5) J. Van Den Berghe, Ph.D. Thesis, University of Wisconsin, 1952.

(6) R. C. Fuson, L. J. Armstrong, and W. J. Shenk, Jr., *J. Amer. Chem. Soc.*, **66**, 964 (1944).

(7) Distilled ethereal diazomethane prepared from N-methyl-N-nitrosourethan contained an impurity in trace amounts leading to the chloromethyl ketone. This impurity was removed by treatment with sodium ribbon and redistillation (see Experimental Section for procedure, also ref 5). The significance of these and related findings to the mechanism of diazo ketone and chloromethyl ketone formation has been discussed in theses.[5,8,9]

(8) C. E. Hummel, Ph.D. Thesis, University of Wisconsin, 1956; *Dissertation Abstr.*, **16**, 2305 (1956).

(9) N. F. Woolsey, Ph.D. Thesis, University of Wisconsin, 1961; *Dissertation Abstr.*, **22**, 3000 (1962).