Anal. Calcd for $C_{10}H_{12}O_7N_2S$: C, 39.47; H, 3.98; N, 9.21. Found: C, 39.76; H, 4.10; N, 8.96.

The other two products were obtained as a yellow crystalline mixture (0.06 g) of **36** and **37** in a ratio 1:1. The ir spectrum ($CHCl_3$) showed the presence of an ester group (1705 cm^{-1}) and a nitro group (1580 and 1295 cm^{-1}). The nmr spectrum ($CDCl_3$) showed two series of signals due to **33** and except for the common signals of the ethoxyl group which appear at τ 5.74 (q, 2 H, J = 6 Hz) and 8.68 (t, 3 H, J = 6 Hz): the signals for **33**, τ 1.24 (s, 0.5 H, Hc), 3.93 (s, 0.5 H, Ha), 6.02 or 6.07 (s, 1.5 H, SCH_3), 7.47 (s, 1.5 H, ring CH_3); the signals for **34**, τ 2.15 (d, 0.5 H, J = 10 Hz, Hc), 3.70 (d, 0.5 H, J = 10 Hz, Hb), 6.07 or 6.02 (s, 1.5 H, SCH_3), 7.22 (s, 1.5 H, ring CH_3).

Registry No.—**3**, 33884-41-2; **4**, 3788-94-1; **5**, 5367-24-8; **6**, 49836-26-2; **7**, 49836-27-3; **8**, 52873-52-6; **9**, 16806-88-5; **10**, 19956-89-9; **11**, 52873-53-7; **12**, 52873-54-8; **13**, 29172-08-5; **14**, 87-13-8; **15**, 49836-33-1; **16**, 49836-32-0; **17**, 21014-78-8; **18**, 49836-34-2; **23**, 7380-81-6; **24**, 52873-55-9; **30**, 52873-56-0; **31**, 52873-59-3; **32**, 34842-62-1; **33**, 52873-57-1; **34**, 591-09-3; **35**, 52873-60-6; **36**, 52873-58-2; **37**, 52873-61-7.

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Simple Deaminations. V.[1–3] Preparation and Some Properties of *N*-Alkyl-*N*,*N*-disulfonimides[4]

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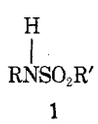
A simple two-step derivatization procedure for the preparation of a variety of *N*-alkyl-*NN*-disulfonimides (**2**) from the parent amines and sulfonyl chlorides is presented. Yields of up to 99% have been obtained. The diarylsulfonimides **2** are in general stable, crystalline solids. The synthetic procedure was developed since these compounds have been observed to undergo facile and synthetically useful deamination. Some ir and pmr properties of these novel compounds are presented and discussed here. In various respects, the disulfonimides **2** behave analogously to the alkyl halides and alkyl pseudohalides.

Whereas numerous references to the preparations and properties of a large variety of *N*-alkyl- and *N*-aryl-monosubstituted sulfonamides (**1**) exist in the literature,[6b,37–46] references to the preparations or properties of *N*-aryl- or *N*-alkyl-*N*,*N*-disulfonimides (**2**)[4] are by comparison



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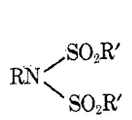
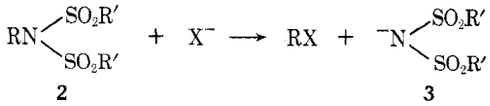


2

rare.[47,48] Thus sulfonamide derivatives (**1**) have long been used in the analysis of amines,[38,39] as protecting groups for amines,[42,43] and in pharmacology.[44] Some of the properties of sulfonamides have been reviewed[41] and good procedures for the preparation of sulfonamides (**1**) are known.[6,37–41] But, until our investigations, only a few scattered reports[15,49–50,57] of the intentional synthesis of *N*-alkyl- or *N*-aryldisulfonimides (**2**) had appeared; several others[51–53] considered disulfonimides as bothersome side products in the characterization or separation of primary and secondary amines by the Hinsberg method.[54] To date, apparently the most "useful" property of disulfonimides **2** is the property first predicted[56] and generally observed[1–3] in our laboratories, that the disulfonimides **2** undergo carbon–nitrogen bond cleavage in the presence of nucleophiles (eq 1).



(1)

2 **3**

That the disulfonimide anions **3**[57] are good leaving groups is predicted from consideration of the pK_a values of the conjugate acids. Thus, for example, the pK_a of *N*,*N*-di(*p*-nitrobenzene)sulfonimide is 0.30.[27] The pK_a values of the parent amines, on the other hand, are in the range of *ca.* 35.[56,59] Our initial successful demonstrations of this new nucleophilic substitution deamination (eq 1) supplied mo-

Table I
Yield and Melting Point Data for Various *N*-Alkylsulfonamides[a]

Compd	Registry no.	R	R′	Yield,[b] %	Mp, °C (Bp, °C/mm)	Lit. mp, °C	Recryst. solvent[c]
1a	1143-01-7	$CH_3(CH_2)_5$	p-$CH_3C_6H_4$	97.3	61.5–62	61[d,e]	Ligroin
1b	7250-80-8	$CH_3(CH_2)_5$	C_6H_5	83.0[f]	[g]		
1c	52374-16-0	$CH_3(CH_2)_5$	p-BrC_6H_4	91.7	54–55	54[d,e]	Ligroin
1d	52374-17-1	$CH_3(CH_2)_5$	m-$NO_2C_6H_4$	61.0[f]	62–63.5	64.5–65.5[d,e]	EtOH–H_2O (4:1)
1e	52374-18-2	$CH_3(CH_2)_5$	p-$NO_2C_6H_4$	97.8	70.4–71.5	70[d,e]	EtOH
1f	52374-19-3	$CH_3(CH_2)_5$	CF_3[h]	97.0	(86–88/0.45)		
1g	52374-20-6	dl-$CH_3CH(CH_2)_4CH_3$	p-$NO_2C_6H_4$	98.7	67.5–68.5		EtOH
1h	52374-21-7	$CH_3(CH_2)_7$	p-$NO_2C_6H_4$	93.1	76–77	75–75.5[d]	EtOH
1i	52374-22-8	dl-$CH_3CH(CH_2)_5CH_3$	p-$NO_2C_6H_4$	78.0[f]	[g]		
1j	52374-22-9	$CH_3(CH_2)_4$	p-$NO_2C_6H_4$	78.5[f]	89.0–90.0[i]	63[d,e]	EtOH
1k	17875-25-1	$(CH_3)_2CH(CH_2)_2$	p-$NO_2C_6H_4$	76.3[f]	88.0–88.6		EtOH
1l	52374-24-0	$C_6H_5CH_2CH_2$	p-$NO_2C_6H_4$	84.9[f]	92.5–93.5		EtOH
1m	52374-25-1	$C_6H_5CH_2$	p-$NO_2C_6H_4$	81.6[f]	126.0–128.8		Aq acetone
1n	80-30-8	C_6H_{11}[j]	p-$CH_3C_6H_4$	93.7	86.0–87.5	85.5–86.4[k]	Aq EtOH
1o	7454-76-4	C_6H_{11}	p-BrC_6H_4	94.0	102.0–102.5		EtOH–H_2O (3:2)
1p	52374-26-2	C_6H_{11}	p-$NO_2C_6H_4$	90.7	136.5–137.5	135–137[l]	MeOH
1q	2849-81-2	$(CH_3)_3C$	p-$CH_3C_6H_4$	97.5	112–113	113.5[m]	EtOH

[a] All structures assigned, particularly for previously unreported compounds, are supported by at least one of the following: melting point, ir, proton nmr, or combustion analysis. Additionally compounds **1a–p** were each further derivatized to the corresponding disulfonimides which were themselves thoroughly characterized. (Tables II and III). [b] These values represent isolated yields based usually on the parent amine as limiting reagent except where noted. Although the highest available yields are listed, they are not atypical of mean values for many runs of individual preparations using optimized procedures. [c] Where ethanol is noted the 95% material can suffice. Solvent mixtures are in v:v proportions; in cases where unspecified proportions of aqueous co-solvents are used, water is added (to a cloud point) to the boiling solution of sulfonamide in organic co-solvent. [d] R. Sasin, *et al.*, *J. Amer. Oil Chem. Soc.*, 37(1), 152 (1960). [e] Reference 6. [f] Yield not optimized, usually the result of only one or two trials. Particularly in these cases, the yield is based on the arylsulfonyl chloride as limiting, where the amine was from 10–20 mol % in excess. [g] This sulfonamide was isolated as an unrecrystallized oil at ambient temperatures; its recrystallization and melting behavior were not further pursued. [h] Table II, footnote *g*. [i] **1j**, although reported in the literature[d,e] to be considerably lower melting, had the properties noted. [j] R for **1n–p** is cyclohexyl. [k] R. F. Carson, *J. Amer. Chem. Soc.*, **75**, 4302 (1953). [l] N. S. Corby, *et al.*, *J. Chem. Soc.*, 1234 (1952). [m] R. N. Lacey, *ibid.*, 1639 (1960).

tivation for development of a simple, efficient procedure to prepare these disulfonimides **2**.

Results

A variety of these symmetrical, *N*-alkyl-*N,N*-disulfonimides **2** have been prepared utilizing an essentially two-step sulfonylation procedure (Scheme I). Sulfonamides **1**

Scheme I

$$RNH_2 + ClSO_2R' \xrightarrow[OH^-]{DMF\text{–}water} \underset{\mathbf{1}}{RNHSO_2R'} + HCl$$

$$RNHSO_2R' \xrightarrow[DMF]{NaH} \left[\begin{matrix} RN\overline{S}O_2R' \\ Na^+ \end{matrix}\right] + H_2 \xrightarrow[DMF]{ClSO_2R'}$$

$$\underset{\mathbf{2}}{RN(SO_2R')_2} + NaCl$$

were prepared in 76–99% yields, utilizing standard procedures (with or without small modifications)[6a,37–40] (see Table I).

The best procedures for preparing disulfonimides **2** were developed *via* trial and error. The best results were obtained *via* the *in situ* generation of the sodium salt of the *N*-alkylsulfonamide in *N,N*-dimethylformamide (DMF), followed by treatment of this soluble sodium salt with 1 equiv of the appropriate sulfonyl chloride; these conditions led to up to *ca.* 99% yields of **2** (Table II). A strong base like sodium hydride was used, since not all sulfonamides react readily or quantitatively with bases like NaOH or KOH; this is not surprising, since the Hinsberg test is, after all, limited.[52b,60]

No examples of disulfonimides **2** derived from primary amines attached to tertiary carbons appear in Table II. Attempts to synthesize the simplest tertiary case, *N*-*tert*-butyl-*N,N*-di(*p*-toluene)sulfonimide, were unsuccessful, even though the corresponding sulfonamide was prepared in 97% yield and the generation of the sodium salt in DMF apparently proceeded smoothly. Subsequent further tosylation at *ca.* 50–60° and normal work-up (quenching the reaction mixture in water) yielded only diminished yields of impure starting sulfonamide. Although no thorough, quantitative work-ups were done in these attempts, it now seems apparent that either there was steric hindrance to disulfonylation or the organic material was lost *via* intermediate disulfonimide formation followed by thermal elimination to isobutylene and *N,N*-di(*p*-toluene)sulfonimide. Hendrickson, *et al.*,[32] have in fact recently found this reaction to be quite facile when utilizing the *N,N*-di(trifluoromethane)sulfonimide ("triflimide") leaving group; in this instance isobutylene elimination was quantitative even at −78°.

Two desirable (if not essential) criteria for practical synthetic intermediates is that they be easily purified crystalline solids, and that they be stable enough to have extended shelf lives at ambient temperatures. All the compounds we have so far isolated have met both these criteria (with the partial exception of the liquid **2f**).

Discussion

Some distinctive spectral properties of the disulfonimides **2** are indicated in Table III. The most characteristic infrared absorption bands exhibited by all the disulfonimide compositions studied here were the very strong symmetric (1155–1170 cm^{-1}) and asymmetric (1350–1385

Table II
Yield and Melting Point Data for Various *N*-Alkyl-*N*,*N*-disulfonimides

Compd[a]	Registry no.	R	R′	Yield,[b,c] %	Mp, °C[d] (Bp, °C/mm)	Recryst. solvent[e]
2a	24332-41-0	$CH_3(CH_2)_5$	$C_6H_4CH_3$-*p*	99.8	114.9–115.2	MeOH
2b	52374-05-7	$CH_3(CH_2)_5$	C_6H_5	86.5[f]	72.5–73.0	EtOH
2c	52374-06-8	$CH_3(CH_2)_5$	C_6H_4Br-*p*	97.0	99.8–100.0	EtOH
2d	52374-07-9	$CH_3(CH_2)_5$	$C_6H_4NO_2$-*m*	77.7[f]	113.0–114.5	EtOH–acetone (4:1)
2e	24332-42-1	$CH_3(CH_2)_5$	$C_6H_4NO_2$-*p*	97.8	132.8–133.1	EtOH
2f	35920-58-2	$CH_3(CH_2)_5$	CF_3[g]	52.0	(50–52/0.04)	
2g	52374-08-0	*dl*-$CH_3CH(CH_2)_4CH_3$	$C_6H_4NO_2$-*p*	86.0[f]	129.0–131.0	EtOH–acetone (1:1)
2h	52374-09-1	$CH_3(CH_2)_7$	$C_6H_4NO_2$-*p*	88.5[f]	134.6–135.0	EtOH–acetone (5:1)
2i	52374-10-4	*dl*-$CH_3CH(CH_2)_5CH_3$	$C_6H_4NO_2$-*p*	46.2[f]	142.0–143.0	EtOH
2j	52374-11-5	$CH_3(CH_2)_4$	$C_6H_4NO_2$-*p*	87.1[f]	149.5–150.0	EtOH
2k	52374-12-6	$(CH_3)_2CH(CH_2)_2$	$C_6H_4NO_2$-*p*	82.4[f]	164.5–165.5	EtOH
2l	52374-13-7	$C_6H_5CH_2CH_2$	$C_6H_4NO_2$-*p*	88.5[f]	166.0–167.0	Acetone–EtOH (2:1)
2m	52374-14-8	$C_6H_5CH_2$	$C_6H_4NO_2$-*p*	94.8	216.0–216.8	Acetone
2n	24332-43-2	C_6H_{11}[h]	$C_6H_4CH_3$-*p*	80.0[f]	159.0–161.0	Acetone
2o	52374-15-9	C_6H_{11}	C_6H_4Br-*p*	81.7[f]	189.0–190.0	Dioxane–water (9:1)
2p	24332-44-3	C_6H_{11}	$C_6H_4NO_2$-*p*	96.0	193.0–195.0	$CHCl_3$–MeOH (3:1)

[a] All compounds in this table are previously unreported except briefly in earlier papers in the series[1-3] and compound **2f**.[30] [b] Highest isolated yield based on the corresponding sulfonamide as limiting reagent, after purification; the per cent yield listed is not atypical of average yields normally obtained over numerous runs of any individual preparation. [c] Preliminary preparations of the *N*,*N*-di(*p*-toluene)- and di(*p*-nitrobenzene)sulfonimides of ethyl alanine indicate that yields for these cases might be considerably lower (*ca.* 30%) than those reported here. [d] All gave clear, clean melts without evidence of decomposition. [e] Where ethanol is specified, the 95% azeotropic material can suffice. [f] In general these were clean, good-yielding reactions, but no particular effort was made to optimize either yields or recrystallization solvent. [g] The sulfonylating agent in this case was trifluoromethanesulfonic acid anhydride, itself prepared from CF_3SO_3H by the method of Granstad and Hazeldine [*J. Chem. Soc.*, 4069 (1957)]. Over five trials the yield for the anhydride averaged *ca.* 47%, the best yield being 61%. [h] Cyclohexyl.

Table III
Physical Data for Various *N*-Alkyl-*N*,*N*-disulfonimides

Compd	Ir[a] SO_2, cm^{-1} (solvent)	Proton nmr[b] $-CH_2N<$ δ, ppm	Empirical formula	Anal. Calcd %C	Calcd %H	Calcd %N	Found %C	Found %H	Found %N
2a	1165, 1378 ($CHCl_3$)	3.61	$C_{20}H_{27}NS_2O_4$	58.65	6.64	3.42	58.57	6.68	3.41
2b	1170, 1380 ($CHCl_3$)	3.69	$C_{18}H_{23}NS_2O_4$	56.67	6.08	3.67	56.72	6.04	3.59
2c	1170, 1380[c] ($CHCl_3$)	3.58[d]	$C_{18}H_{21}NS_2O_4Br_2$	40.09	3.92	2.60	40.23	3.91	2.58
2d	1175, 1371[e] (KBr)	3.77	$C_{18}H_{21}N_3S_2O_8$	45.85	4.49	8.91	45.61	4.56	8.70
2e	1170, 1350–1380[f] ($CHCl_3$)	3.70	$C_{18}H_{21}N_3S_2O_8$	45.85	4.49	8.91	45.85	4.45	8.90
2f	1190, 1382 (neat)	3.98	$C_8H_{13}NS_2O_4F_6$	26.30	3.59	3.83	26.48	3.82	3.63
2g	1170, 1350–1365[c] (CCl_4)	4.35[g]	$C_{19}H_{23}N_3S_2O_8$	47.00	4.78	8.65	47.08	4.64	8.72
2h	1155, 1350[c] ($CHCl_3$)	3.80	$C_{20}H_{25}N_3S_2O_8$	48.09	5.04	8.41	47.85	4.97	8.19
2i	1165, 1350[c] (KBr)	4.30[g]	$C_{20}H_{25}N_3S_2O_8$	48.09	5.04	8.41	48.11	5.03	8.42
2j	1160, 1345–1380[f] ($CHCl_3$)	3.70	$C_{17}H_{19}N_3S_2O_8$	44.63	4.19	9.19	44.44	4.19	9.03
2k	1171, 1385 (KBr)	3.80	$C_{17}H_{19}N_3S_2O_8$	44.63	4.19	9.19	44.51	4.24	9.25
2l	1170, 1380 (KBr)	4.14[h]	$C_{20}H_{17}N_3S_2O_8$	48.88	3.49	8.55	49.00	3.60	8.56
2m	1170, 1385 (KBr)	5.02[i]	$C_{19}H_{15}N_3S_2O_8$	47.80	3.17	8.80	47.71	3.21	8.84
2n	1170, 1375[c] (KBr)	3.95[g]	$C_{20}H_{25}NS_2O_4$	58.96	6.18	3.44	58.94	6.24	3.41
2o	1165, 1375 ($CHCl_3$)	4.00[g]	$C_{18}H_{19}NS_2O_4Br_2$	40.24	3.56	2.61	40.13	3.55	2.71
2p	1170, 1355[c] ($CHCl_3$)	4.08[g]	$C_{18}H_{19}N_3S_2O_8$	46.06	4.08	8.95	45.96	4.05	8.89

[a] See Discussion below, especially with regard to the asymmetric SO_2 vibration. [b] All spectra were obtained in deuteriochloroform unless otherwise noted. All α-methylene absorptions were sharp triplets; α-methine absorptions were in general roughly first-order multiplets. [c] Broad envelope with multiple shoulders; wavenumber listed is at approximate center of peak. [d] In CCl_4. [e] Resolved absorbances also at 1350 and 1364 cm^{-1}. [f] Multiple strong, unresolved absorbances. [g] Methine proton. [h] In DMSO-d_6. [i] Benzyl protons.

cm^{-1}) stretching modes of the SO_2 group. The corresponding frequencies for the well-known N-substituted sulfonamides are widely quoted[61a,62a-65] to be in the ranges of *ca.* 1140–1180 cm^{-1} and *ca.* 1300–1350 cm^{-1}, respectively (*cf.* also Table IV). Perusal of Table III will indicate that, whereas the symmetric SO_2 vibrational frequencies of compounds **2a–2p** are about the same as those quoted for sulfonamides, the asymmetric SO_2 vibrational frequency is shifted to shorter wavelengths by as much as 20–30 cm^{-1}. Hypsochromic shifts of 10–20 cm^{-1} above the normal 1322–1334-cm^{-1} range[64] for the asymmetric SO_2 mode of *N*-alkylsulfonamides are common[61a,62a,65] when spectra are recorded in solution (CCl_4 or CS_2) instead of the solid state (KBr). This has been attributed[65] to strong association (presumably dimeric hydrogen bonding) of N-monosubstituted sulfonamides in solution. Since compounds **2** lack amino protons and furthermore have asymmetric SO_2 stretching frequencies even higher than other N,N-disubstituted sulfonamides,[66] it is likely that the hypsochromic shift observed is due to other factors peculiar to the sul-

Table IV
Some Physical Properties of Various *N*-Alkylsulfonamides

Compd	Ir SO_2 frequencies, cm^{-1} Symmetric	Asymmetric	Solvent	Proton nmr[a,b] δ, ppm >NCH_2–	NH[d]
1a	1160	1330	$CHCl_3$	2.92[c] (q)	5.90 (t)
1b					
1c	1162	1340	CCl_4		
1d	1170	1350	CCl_4	2.98[c] (q)	5.55 (t)
1e	1165	1350	$CHCl_3$	3.02 (q)	5.50 (t)
1f	1190	1340	neat	3.30 (q)	5.60 (t)
1g	1170	1340	CCl_4	3.15[c] (sx)[e]	5.70 (d)
1h	1150	1340	$CHCl_3$	3.00 (b, q)	5.05 (t)
1i				3.47 (sx)[e]	5.87 (b, s)
1j	1155	1345	$CHCl_3$	2.90 (q)	5.17 (t)
1k					
1l				3.30 (t)	5.00 (b, s)
1m	1150	1340	$CHCl_3$		
1n	1160	1325	KBr	3.15 (b, s)[e]	4.95 (b, s)
1o	1161	1340	$CHCl_3$		
1p	1160	1350	$CHCl_3$		
1q	1150	1330	$CHCl_3$		

[a] All spectra recorded in $CDCl_3$ unless otherwise noted. Chemical shifts are in parts per million from internal TMS. [b] Multiplicity indicated parenthetically by the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, sx = sextuplet, m = multiplet, b = broad. [c] Recorded in CCl_4. [d] In individual cases these absorptions might be slightly solvent or concentration dependent; all signals are easily exchangeable with D_2O without catalysis. [e] Methine proton.

fonimide moiety itself. Specifically it appears that the inherent electron-withdrawing ability of the sulfonyl group is reinforced by the adjacent sulfonamido moiety (and *vice versa*), so that what is seen is an overall relative strengthening of the S–O double bonds as a result of the disulfonyl substitution on nitrogen. Similar shifts to higher frequency (of 10–20 cm^{-1} in magnitude) are also seen for the asymmetric SO_2 in compounds wherein two or three sulfonyl groups are geminally attached to carbon: di- and trisulfonylmethanes in contrast to methylethylsulfone,[67] for example. *N*-Acetylsulfonamides[68] and quaternized sulfonamides[69] also display infrared spectra which indicate that electron-accepting substituents on nitrogen tend to shift the SO_2 frequencies to shorter wavelength regions.

Several additional comments concerning the infrared spectra are noteworthy. Compounds **2d, 2e, 2g–m,** and **2p** are all *N,N*-di(*p*-nitrobenzene)sulfonimides. As a result the spectra display the very strong C–NO_2 stretching frequencies of the nitrobenzene moieties (*ca.* 1527 and 1348 cm^{-1} for the asymmetric and symmetric frequencies, respectively[62b]); the range for the symmetric frequency has been quoted[61b] as 1348 ± 11 cm^{-1}. This latter, broad absorption lies close enough to the asymmetric SO_2 frequency to, in a number of cases (**2e, 2g–j,** and **2p**), merge with it into a broad, intense, unresolved envelope, making precise assignments uncertain. In cases where some resolution is apparent (**2d, 2k–m**), the asymmetric SO_2 frequency has been tentatively assigned to the higher frequency in the 1340–1390-cm^{-1} range in analogy to the diarylsulfonimides of Table III which do not contain aromatic nitro substituents[70] (*cf.* also Table V for similar data on the protonated leaving groups of eq 1). The data also indicate other patterns: (a) the asymmetric SO_2 stretching mode is, in general, more complex than the symmetric one; (b) in contrast to sulfonamides, no obvious effects of solvent or phase in the SO_2 stretching modes are discernible; (c) both the symmetric and asymmetric oscillations of the SO_2 group in compounds **2** are apparently relatively insensitive to both the type and position of substituents on the aromatic ring. Results analogous to the latter generalization are noted for a series of *N*-phenyl-*p*-toluenesulfonamide derivatives.[71]

The C–N stretching frequency of N-substituted sulfonamides is quoted[64] to be 1058–1074 cm^{-1} when the α carbon is primary and 1036–1040 cm^{-1} when the α carbon is secondary. In the compounds of this study, a sharp band of

Table V
Physical Properties of Several Diarylsulfonimides

Compd[a]	Registry no.	R′	Ir frequencies,[b] SO_2, cm^{-1}		Proton nmr[c,d] δ, ppm NH[e]	Aromatic[f]	Formula	Anal. Calcd %C	%H	%N	Found %C	%H	%N
3a	3695-00-9	*p*-$CH_3C_6H_4$[g]	1165	1360	10.51 (s, 1 H)	7.48 (q, 8 H, J_{ab} = 8.5 Hz)	$C_{14}H_{15}NS_2O_4$	51.68	4.65	4.30	51.72	4.60	4.38
3b	1156-18-9	*p*-BrC_6H_4[h]	1160	1370	8.74 (s, 1 H)	7.60[i] (q, 8 H, J_{ab} = 8 Hz)	$C_{12}H_9NS_2O_4Br_2$	31.67	1.99	3.08	31.50	2.12	2.93
3c	2618-96-4	C_6H_5[j]	1165	1360	12.17 (s, 1 H)	7.62 (m, 10 H)	$C_{12}H_{11}NS_2O_4$	48.47	3.73	4.71	48.35	3.68	4.65
3d	4009-06-7	*p*-$NO_2C_6H_4$[k]	1155	1380[l]	11.33 (s, 1 H)	8.10 (q, 8 H, J_{ab} = 8 Hz)	$C_{12}H_9N_3S_2O_8$	37.21	2.34	10.55	37.15	2.33	10.89
3e	52374-27-3	*p*-$NO_2C_6H_4$[m]	1155	1375[n]	Absent	8.10 (q, 8 H, J_{ab} = 8 Hz)	$C_{12}H_8N_3S_2O_8K$	33.81	1.89	9.86	33.86	1.94	9.98

[a] Compounds 3a–e are the protonated leaving groups of eq 1; 3e is the potassium salt of 3d. 3a–e, although isolated from deamination reactions, were identical in all respects with known compounds synthesized by alternative means.[57] [b] All spectra recorded as KBr pellets (*ca.* 1% by wt). [c] All spectra recorded in DMSO-d_6. [d] Chemical shifts are in ppm downfield from internal TMS. [e] These absorptions may be both solvent and concentration dependent; all are easily exchangeable with D_2O. [f] Except for 3c all spectra display symmetrical AA′BB′ quartets, with coupling constants in hertz given parenthetically following the multiplicity. [g] Mp 168–169° [lit. mp 169°, German Patent 1,222,058; *Chem. Abstr.*, **66**, 2228n (1967)]. [h] Mp 232–233° (lit. mp 232–233°, ref 22a). [i] This absorption is a limiting AA′BB′ quartet whose outermost members are much diminished in intensity compared to the innermost members, which form a closely spaced doublet. [j] Mp 156–157° [lit. mp 157.5–158.5°, G. R. Pettit and R. E. Kadunce, *J. Org. Chem.*, **27**, 4567 (1962)]. [k] Mp 240–241° (lit. mp 241°, ref 12). [l] Assignment tentative; strong absorptions also at 1348 and 1365 cm^{-1}. [m] Mp 270–272°. [n] Part of a broad envelope.

weak to medium intensity was noted for each at *ca.* 1020–1045 and 1014–1025 cm^{-1} for α-primary and α-secondary compounds, respectively. These considerable shifts to shorter wavelength appear to be consistent with the expected and demonstrated[1-3,29-32] relative weakness of the C–N bond in compounds containing the sulfonimide group. Another sharp band of medium intensity which is consistently elicited in compounds **2** occurs in the 1082–1092-cm^{-1} region. Although earlier suggestions have assigned this band to S–N stretching[65] or aromatic C–H bending[62c] vibrations, it is now more properly assigned[64] to the C–S stretching vibration.

The proton magnetic resonance spectra of compounds containing the sulfonimide group display some interesting characteristics, the most distinctive feature being the marked downfield chemical shifts for hydrogen α to the sulfonimide moiety. Typical values occur at *ca.* 3.6–3.8 ppm for methylene protons, *ca.* 4.0–4.3 ppm for methine protons, and as high as 5.0 for benzylic protons. Among the more typically encountered functional groups, only aryloxy, ester, nitro, and fluorine substituents give rise to chemical shifts for α-methylene protons greater than the sulfonimide group, which causes shifts even larger (by some 0.2–0.4 ppm) than chloride, bromide, or iodide.[72a] Specifically with regard to α-methylene protons of primary alkyl groups, the shift ascribed to the electron-withdrawing power of the sulfonimide group is at least 0.7–0.8 ppm further downfield than that produced by the corresponding sulfonamides (*cf.* Table IV) which themselves display α-hydrogen shifts that are 0.3–0.4 ppm more deshielded than the parent amines.[73]

Relative to other nitrogen-containing derivatives, the shifts induced by the sulfonimide group on α-aliphatic protons are considerably larger than those elicited in N-alkylated amides (*ca.* 3.2 ppm[72a]) and are more properly compared in magnitude to those caused by *N,N*-diarylamino- (3.6–4.0 ppm[74]), phthalimido (3.5–3.9 ppm[75]), and 1,2-benzisothiazolin-3-one 1,1-dioxide (saccharin-derived, 3.6–3.98 ppm[76]) groups.

On the basis of this evidence, it might be supposed that the effective group electronegativity of the sulfonimide moiety is at least in the category of the common halides or pseudohalides. There have, of course, been extensive efforts to correlate chemical shifts with inductive effects or electronegativities of substituents.[77,78] More recently Price[79] has elicited empirical rules which correlate pmr chemical shifts for hydrogens α to lone-pair electrons. A consequence of this approach is to account for the steric environments which bring α hydrogens closer to the lone pair(s) on the substituents, thereby shifting their pmr signals further downfield; accordingly enhanced steric hindrance in secondary compounds would produce an augmented increment in downfield shift. These trends, well known for other substituents (like halides, esters, ethers, amines, etc.),[81a] are in agreement for sulfonimide-containing compounds, with downfield shifts of *ca.* 0.4–0.7 ppm (see Table III) being noted for geminal methine protons *vs.* methylene protons. Whatever the actual contributory factors or physical bases are for the trends and magnitudes of the pmr shifts noted, these spectral changes are further qualitative substantiation of the structural or electronic similarity of the sulfonimide moiety to other substituents which are good nucleophilic displacement leaving groups.

The spin–spin multiplicity of protons (methylene or methine) geminal to sulfonimido nitrogen are, in general, in accord with first-order spectra rules, with distinct patterns indicative of neighboring protons and coupling constants in the range of *ca.* 7–9 Hz. (All triplets observed for α-methylene protons showed slightly asymmetric enhancement of their high-field components indicating coupling to β-methylenes.) The sulfonimide substituents also consistently gave rise to β-methylene shifts in the order of *ca.* 1.7 ppm. Furthermore, all the para-substituted diarylsulfonimides **2** display easily discernible, characteristically symmetrical AA′BB′ quartets in the aromatic region; the remaining protons are accounted for by more complex aliphatic multiplets.

Of the ten pmr spectra of sulfonamides **1** noted in Table IV, at least seven showed relatively sharp, distinct absorptions for the N–H protons and easily observable H–N–C–H pmr spin–spin coupling. In the compounds having α-methylenes, for example, the N–H protons displayed triplets ($J_{HNCH} \simeq$ 5–6 Hz) while the methylene protons exhibited quartets whose low-field components were slightly broadened and skewed. Upon uncatalyzed D_2O exchange, the N–H absorptions would disappear virtually instantly while the methylene quartets collapsed to triplets. Resonance signals for hydrogen on amines, amides, and imides are commonly broad and sometimes even unobservable,[72b,81b,82] owing to various factors which include interaction with the electric quadrapole moment of nitrogen, intermediate rates of exchange, trace impurities which catalyze exchange processes, etc. Acid-catalyzed exchange processes would be expected to be slow because of the reduced basicity of the sulfonamide nitrogen (sulfonamides are themselves actually relatively acidic, of course, with pK_a values in the range of *ca.* 8–10[56]). Alkaline catalysis of proton exchange might be a cause for some of the sharpening, but even if this is the case, the exchange was apparently never rapid enough to smear the H–N–C–H spin–spin interactions. Although no definitive pmr experiments were performed to elucidate the precise cause for the sharpened, yet coupled absorbances, these observations might be due to a fortuitous combination of factors including optimum observational temperatures,[83] structural influences, and/or conditions for the minimization of quadrapole relaxation. In addition the data in Table IV do not suggest any obvious relation of J_{HNCH} to either the electron-withdrawing ability of the nitrogen substituent or the chemical shift of the protons geminal to nitrogen, although such a (linear) relationship has been noted for a family of N-substituted methylamines.[84] One additional point of interest concerning hydrogen bound to nitrogen is that the known acidities (pK_a values *ca.* 0.3–3.0)[27] of sulfonimide (**3a–e**) hydrogens are apparently verified by their strongly deshielded chemical shifts (see Table V); these values place them in the category of carboxylic (δ 10–13) and sulfonic (δ 11–12) acids.[81b]

The key chemical property, responsible for our interest in **2a–p,** was briefly alluded to earlier (eq 1, aliphatic nucleophilic displacement at carbon bearing nitrogen), and has been[1-3] and will be discussed in other publications in this series. With respect to C–N cleavage reactivity, probably the best deaminative substrate to date[1,2,30,32] in this family is **2f** since it gives high, clean yields of substitution products under exceedingly mild conditions and short reaction times. On economic and convenience bases however, the most ideal of the dibenzenesulfonimides have been the di(nitrobenzene)sulfonimides, since they still give exceedingly pure substitution products in excellent yields and at the fastest rates[1,2] relative to other diarylsulfonimides tested. The diarylsulfonimides **2** are apparently not particularly susceptible to solvolyses (see Table II); they have been routinely recrystallized from lower boiling alcohols (some containing water) without decomposition or significant losses. The disulfonimides can also undergo partial saponification under more stringent conditions. This reaction constitutes a complication when nucleophilic substitution

is attempted with stronger bases such as cyanide, hydroxide, or mercaptide in polar aprotic media. With sulfonamides usually the reverse is true, wherein they are hydrolyzed by acids (though less readily than sulfonyl halides or sulfonate esters), but are not generally hydrolyzed by alkaline treatment.[85] (Examples of base-catalyzed sulfonamide alcoholyses have been reported.[86]) In contrast the N–S bond of the disulfonimides **2** appears to be relatively stable to acid-catalyzed hydrolysis; under acid conditions, in fact, virtually quantitative C–N cleavage has been realized.[87]

Experimental Section

Materials. All chemicals used in these preparations were reagent grade or better and supplied from the following firms: Aldrich Chemical Co., Milwaukee, Wis., Eastman Kodak Co., Rochester, N.Y., The J. T. Baker Co., Phillipsburg N.J., Fisher Scientific Co., Pittsburgh, Pa., and Sargent-Welch Scientific Co., Skokie, Ill. Deuterated pmr solvents were supplied by Diaprep, Inc., Atlanta, Ga. NaH was purchased as a 50–58% oil dispersion from K & K Laboratories, Plainview, N.Y. CF_3SO_3H was obtained from the 3M Co., Chemical Division, St. Paul, Minn. *dl*-2-Aminooctane was prepared[88] by the sodium in ethanol reduction of the corresponding methyl *n*-hexyl ketoxime.

Instrumentation. Melting points (uncorrected) were determined in soft, open capillary tubes using a Buchi Schmelzpunktbestimmungapparat equipped with a silicone fluid bath and an NBS thermomenter. Infrared (ir) specta were run on either a Perkin-Elmer 521 or a Beckman IR-10 spectrometer, using spectrophotometric grade reagents (solvents or KBr), and calibrated *vs.* polystyrene. Proton nmr (pmr) spectra were recorded on Varian Associates A-60A and T-60 analytical nmr spectrometers. All chemical shifts are reported in ppm downfield from internal TMS and are assumed correct to ±0.02 ppm.

Analytical gas–liquid partition chromatography (glpc) was performed on an F & M Scientific Hewlett-Packard Model 407 high-efficiency gas chromatograph using nitrogen as a carrier gas. All columns were ⅛ in. (o.d.) × 6 in. Pyrex U-tubes, and all solid supports were acid washed, DMCS treated. Purity of amines was routinely assessed by glpc using a 10% Carbowax 20M/KOH impregnated on 60/80 mesh Chromosorb W column. **1f** and **2f** or mixtures thereof, were analytically separable on the following columns: 10% QF-1 on 60/80 Chromosorb W, 10% SE-30 and 10% DEGS, both on 80/100 Chromosorb W. In all cases the more highly fluorinated compound, **2f**, had the shorter retention time.

Elemental microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Galbraith Laboratories, Inc., Knoxville, Tenn.

General Synthetic Methods. Since the preparations of the *N*-alkylsulfonamides in this study are similar in many aspects to older preparations, only the most salient, yield-maximizing features will be outlined. All reactions described, for the higher-boiling aliphatic amines, can conveniently be conducted in open beakers or erlenmeyer flasks on magnetic-stirring hot plates.

Generally a dilute solution (*ca.* 10–20% by wt) of the primary amine is made in water or aqueous DMF as solvent; the proportion of DMF used (from none to 15% by vol) is dependent only on the solubility of the parent amine. To this stirred solution of amine is then added the appropriate sulfonyl chloride (in equimolar or up to 10% excess proportions) in three to five portions, each in 10- to 15-min intervals, with alternating basicifications using concentrated (20–50% by wt) aqueous base (use of KOH or NaOH is interchangeable). Throughout these simultaneous, but alternating, addition steps, the pH is monitored (pH meter or more simply with pHydrion paper); pH changes can conveniently be used as cues for the next addition. In total, no more than 1 equiv of base is necessary. During the course of the sulfonylation–basicification procedure, the reaction temperature typically is allowed to either exotherm or be externally raised to *ca.* 80–90°. These temperatures, even though they exceed the melting points of some of the aromatic sulfonyl chlorides or sulfonamides involved and can cause the oiling out of the reactant–product mass, have been shown not to be detrimental to the overall procedure. When all the additions are complete, the reactants are stirred for an additional 0.5 hr, the mixture cooled in ice, acidified with concentrated HCl with stirring, and cooled further (with scratching if necessary). The solid thus obtained is filtered, washed with a large excess of water, and recrystallized from the appropriate solvent (see Table I).

The *N*-alkyl-*N,N*-disulfonimides were prepared directly from their corresponding sulfonamides (as limiting reagents), by dissolution in DMF (to make a 15–50% by wt solution), treatment with NaH (oil dispersion), then further reaction with another equivalent of corresponding sulfonylating reagent. During the course of the salt formation, more DMF can be added as necessary to retain homogeneity and to fully dissolve the salt; all *N*-alkylsulfonamide sodium salts encountered were DMF soluble, and yields are sensitive to complete generation and dissolution of them. Excess NaH can be used to ensure complete reaction or take account of any residual water in the DMF. Use of NaH as an oil dispersion was done routinely without incident or any particular precautions to avoid exposure to atmospheric oxygen. In the cases of *N,N*-di(nitrobenzene)sulfonimide preparations, the salt formation and sulfonylation steps were attended by intense color changes which are useful indicators of reactivity. Incremental additions of NaH to nitrobenzenesulfonamides elicits yellow to orange to red to dark brown transitions; completion of the subsequent sulfonylation usually produces a cloudy (suspended NaCl) yellow shade again. The crude diarylsulfonimides are isolated by quenching the DMF reaction mixture in water and filtration. For all solid, isolated products (**1** and **2**) it is essential to take two and even three crops from the recrystallizations to ensure maximal yields. The following preparations are typical.

Preparation of *N*-(*n*-Hexyl)-*p*-toluenesulfonamide (1a). To a solution of 212.0 g (2.09 mol) of *n*-hexylamine in 1 l. of 15% DMF–water (v:v) was added 236.0 g of *p*-TsCl (1.24 mol) slowly. Heating was unnecessary as the mixture exothermed to *ca.* 90°. After 15 min the pH of the solution had decreased to *ca.* 3 (pHydrion paper) and was adjusted to pH 8 with 25% aqueous NaOH. This adjustment was followed with a 112.0-g portion of TsCl (0.588 mol). Within 20 min the pH was again *ca.* 3 and readjusted to pH 8 with more 25% NaOH. A final portion of 50.00 g of TsCl (0.262 mol) was added. After 10 min the pH 3 solution was again adjusted to pH *ca.* 9. The reaction mixture was stirred for another 75 min during which time the pH remained approximately constant. Then the reaction mixture was acidified (to pH 3) with 6*N* HCl, cooled in ice with stirring, and the snow-white product crystals filtered, washed, and recrystallized from 2 l. of ligroin. The total yield in two crops was 518.80 g (97.3%), mp 61.5–62° (lit.[6b] mp 62°). Over eight similar trials, yields averaged 93.4%. *Anal.* Calcd for $C_{13}H_{21}NSO_2$: C, 61.14,; H, 8.29; N, 5.48. Found: C, 61.47; H, 8.49, N, 5.46. Ir (CCl_4) showed 3400 (s, b), 2920 (s, b), 2875 (s), 1607 (m, sh), 1390 (s, sh), 1330 (s, b), 1160 (s, b), 1095 (s, b) cm^{-1}.

Preparation of *N*-(*n*-Hexyl)-*N,N*-di(*p*-toluene)sulfonimide (2a). **1a** (50.00 g, 0.192 mol) were dissolved in 100 ml of dry DMF. Then 9.40 g of a 50% NaH oil dispersion (0.196 mol) was added slowly to form the sodium salt of the sulfonamide; gas evolution was apparent. A further addition of *ca.* 150 ml of DMF was made to dissolve the salt completely. After 30 min of stirring, 41.20 g of TsCl (0.216 mol) was added. After an additional 30 min the reaction mixture was poured into 1 l. of water in order to precipitate the crude **2a** which was collected by suction filtration. Since the aqueous DMF filtrate was still cloudy, it was extracted with chloroform; the chloroform was washed with water, and then flash evaporated. The crude **2a** collected in this way was added to that above and the total recrystallized from about 600 ml of MeOH. **2a** was collected in two crops (75.95 and 4.41 g) totaling 80.36 g (99.8%). Over eight similar trials yields averaged 92.9%. **2a** from above had mp 114.5–115°; an analytical sample was prepared by several runs through a zone-refining apparatus to yield a pure white solid, mp 114.9–115.2° *Anal.* Calcd for $C_{20}H_{27}NS_2O_4$: C, 58.65; H, 6.64, N, 3.42. Found: C, 58.57; H, 6.68, N, 3.41. Ir ($CHCl_3$) showed N–H stretching region blank, 2980, 2950, 2880 (m, sh), 1610 (m, sh), 1378 (s, b), 1165 (s, sh), 1090 cm^{-1}. Nmr ($CDCl_3$) had aliphatic region, 0.82–2.0 ppm (m, 11 H), aromatic methyl, 2.30 ppm (s, 6 H), α-methylene, 3.61 ppm (t, 2 H, J = 7–8 Hz), and an aromatic AA′BB′ quartet centered at 7.43 ppm (8 H, J_{ab} = 8 Hz).

Preparation of *N*-(*n*-Hexyl)-*p*-bromobenzenesulfonamide (1c). To a solution of 28.00 g of *n*-hexylamine (0.278 mol in *ca.* 150 ml of water) was added 35.75 g of BsCl (0.140 mol), and the mixture heated to melt the sulfonyl chloride. After 1 hr, 7.80 g of KOH (0.139 mol) in 15 ml of water was added, followed by 17.87 g of BsCl (0.070 mol). After an additional 30 min 7.80 g more of KOH (0.139 mol) in water were added, followed by a final 17.87-g portion of BsCl (0.070 mol). After allowing another 0.5-hr reaction time, the mixture was quenched with concentrated HCl, bringing the pH down to *ca.* 2, precipitating crude **1c**, which was collected by suction filtration and recrystallized from 175 ml of ligroin to yield 81.4 g (91.7%) in two crops. **1c** consisted of pure white, waxy

plates: analytical mp 54–55° (lit.[6b] mp 55°); ir ($CHCl_3$) 3410 and 3300, 2950, 2880 (s, sh), 1590 (m, sh), 1340 (s, b), 1162 (s, sh), and a doublet at 1100–1175 (s, sh) cm^{-1}.

Preparation of N-(n-Hexyl)-N,N-di(p-bromobenzene)sulfonimide (2c). To a solution of 32.025 g of **1c** (0.100 mol) in *ca.* 200 ml of DMF was added 4.22 g of 57% NaH (as an oil dispersion) (0.100 mol). The mixture reacted 1 hr. Then 27.00 g of BsCl (0.106 mol) was added and allowed to react for an additional 0.5 hr. Addition of 300 ml of water precipitated the crude **2c** which was collected and recrystallized from 150 ml of EtOH; 52.33 g (97.0%) of finely divided, pure white solid, mp 98.5–99.5°, was collected in two crops. The average yield for five similar runs was 95.2%. Several runs through a zone-refining apparatus and one recrystallization from 100% EtOH provided an analytical sample, mp 99.8–100.0°. *Anal.* Calcd for $C_{18}H_{21}NS_2O_4Br_2$: C, 40.09; H, 3.92; N, 2.60. Found: C, 40.23; H, 3.91; N, 2.58. Ir spectrum ($CHCl_3$) showed the N–H stretching region blank, 2950 (s, sh), 2895 (m), 1590 (s, sh), 1380 (s, b), 1160 (s, sh), 1020–1095 (s, multiplets) cm^{-1}; nmr (CCl_4) 0.82–1.95 ppm (m, 11 H), 3.58 ppm (t, 2 H, J = 9 Hz), and AA′BB′ quartet centered at 7.56 ppm (8 H, J_{ab} = Hz).

Preparation of N-(n-Hexyl)-p-nitrobenzenesulfonamide (1e). To a stirred solution of 31.0 g of n-hexylamine (0.307 mol) in *ca.* 100 ml of water, in a 300-ml erlenmeyer flask which was maintained at about 70°, was added the first of three portions of NsCl (37.45 g, 0.169 mol). When the reaction mixture became acidic to pHydrion paper, it was made basic again with an aliquot of aqueous NaOH solution. (The product when formed, at or near its melting point, oils out of the reaction mixture as does the NsCl; the two phases can be kept in intimate contact simply by vigorous magnetic stirring.) In a similar stepwise manner, two more 18.73-g (0.0845 mol) NsCl additions and basifications were made over a 1-hr period. The reaction mixture was stirred for an additional 15 min and acidified with concentrated HCl; the flask was cooled in ice. The collected product, recrystallized from 95% EtOH in three crops, totalled 86.1 g (97.8%), mp 69–71°. Subsequent repeated recrystallizations provided an analytical sample, mp 70.4–71.5° (lit.[6a] mp 71°). *Anal.* Calcd for $C_{12}H_{18}N_2SO_4$: C, 50.33; H, 6.34; N, 9.78. Found: C, 50.38; H, 6.33; N, 9.87. Ir ($CHCl_3$) showed 3410 (s), 3310 (m), 2950 (s), 2880 (sh), 1618 (m, sh), 1350 (s, b), 1165 (s, sh), 1098 (s, sh) cm^{-1}.

Preparation of N-(n-Hexyl)-N,N-di(p-nitrobenzene)sulfonimide (2e). Exactly 28.63 g of **1e** (0.100 mol) were dissolved in 150 ml of DMF to give a clear, pale yellow solution, to which was added 5.0 g of 57% NaH (0.119 mol), and allowed to react until the color had changed completely (yellow to red to clear, dark brown transitions) and the evolution of hydrogen had ceased, *i.e.*, about 1.5 hr. As needed more dry DMF was added to dissolve the salt. Then 24.0 g of NsCl (0.109 mol) were added and allowed to react for 1 hr. Precipitation, cooling with scratching, filtration, and recrystallization (EtOH) yielded 46.05 g (97.8%) in two crops after drying over P_2O_5 with mp 132–133°. Yields for seven similar syntheses averaged about 94%. Subsequent recrystallizations provided an analytical sample, mp 132.8–133.1°. *Anal.* Calcd for $C_{18}H_{21}N_3S_2O_8$: C, 45.85; H, 4.49; N, 8.91. Found: C, 45.85; H, 4.45; N, 8.90. Ir ($CHCl_3$) showed 2940 (m, b), 2880 (w, b), 1610 (m, sh), 1530 (w, b), 1350–1380 (s, b), 1170 (s, sh), 1090 (s, sh) cm^{-1}; nmr ($CDCl_3$) showed 0.6–1.9 ppm (aliphatic m, 11 H), terminal methylene at 3.70 ppm (t, 2 H, J = 8.0 Hz), and a poorly coupled, rather broadened AA′BB′ aromatic quartet at 8.19 ppm (8 H).

All other examples of **1** and **2** were made by analogous preparations, yielding similar observations and results which are tabulated in Tables I–IV. Exceptions include **1f** and **2f** which were made in chloroform and diethyl ether, respectively; different approaches were taken with these compounds because the sulfonylating agent was the more reactive anhydride. Although **1f** was obtained in excellent yield, the salt generation and preparation of **2f** were not optimized, and, in fact, by the methods pursued, **2f** was available essentially free of residual **1f** only by fractional, vacuum spinning-band distillation. Apparently more effective preparations of **2f** have been elucidated,[29,30] wherein the disulfonylation is done in one step utilizing the anhydride in the presence of a tertiary amine, but the details of the method have not been disclosed. A one-step disulfonylation, of course, is to be preferred, but it is likely to be applicable only to particularly acidic monoalkylated sulfonamides analogous to **1f** when using the more reactive sulfonic acid anhydride.

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Registry No.—Hexylamine, 111-26-2; *p*-TsCl, 98-59-9; BsCl, 98-58-8; NsCl, 98-74-8.

References and Notes

(1) Part IV: P. J. DeChristopher, G. D. Lyon, J. P. Adamek, R. J. Swedo, S. A. Klein, and R. J. Baumgarten, presented to the Division of Organic Chemistry at the 161st National Meeting of the American Chemical Society, Los Angeles, 1971, ORGN No. 14. Some of the results reported in this paper were given in preliminary form at this meeting and some of the results were mentioned in ref 3.

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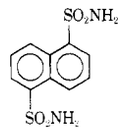
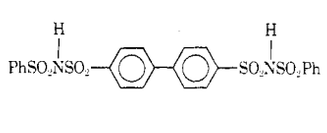
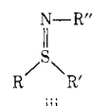
(4) In the past and more recently, a number of investigators have independently named the title compounds here in various ways: disulfonamides,[5a,6,7] disulfonylimides,[9,10] sulfimides[11–13] or disulfimides,[14–18] disulfonimides,[19,20] and sulfonimides.[1–3,29–32] *Chemical Abstracts* guide[5a] and the "IUPAC Nomenclature of Organic Chemistry" (1965) rules[5c] teach the disulfon*a*mide nomenclature. Although this is useful in simpler cases,[8] this nomenclature is either ambiguous or fails in cases of compounds like i or ii for example. (See ref 33, 34 and 50, for example, for other potentially confusing or ambiguous nomenclature examples.) The name sulfimide, although it has been adopted[35] for structures



i



ii



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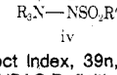
iii (which are more properly called sulfiliminies[5b] and widely misused, particularly in the European patent literature[11–13,15–17] for compounds **2**, is also not sufficiently descriptive for them either. Uniform adoption of "sulfonimide" as a *principal group* suffix is strongly recommended for the description of the $-SO_2NHSO_2-$ functionality; *i.e.*, in compounds where two alkylsulfonyl or arylsulfonyl moieties are attached to the same trivalent nitrogen atom. After this characteristic group has been designated, then the rest of the name is built by the normal substitutive nomenclature rules and priorities. The sulfonimide nomenclature is already preferred in the more practical, less cumbersome American usage.[1–3,29–32] It is practical because it unambiguously specifies the nitrogen to which the sulfonyl groups are attached, as well as the groups attached to sulfonyl groups, and to the third valence of the nitrogen. Additionally the name emphasizes the structural analogy to diacyl-substituted nitrogen compounds like maleimide or phthalimide, while avoiding the use of double naming procedures inherent in that system: *viz.*, $HN(COR)_2$ could be called a diacyl*amine*, but an N-substituted relative, $RN(COCH_3)_2$, would be called an N-substituted diacetamide. In naming symmetrical sulfonimides, *i.e.*, those which have identical aryl or alkyl moieties attached to the sulfonyl groups, it is generally more informative to use the "N,N-di-" prefix to uniquely specify this situation. The use of this prefix is further reinforced by the recent introduction[36] into the literature of the trivial name "sulfonimide" to describe sulfonylaminimides, iv.



iv

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