140-88-5; **14a**, 78782-02-2; **14b**, 78782-03-3; **14c**, 78782-04-4; **15a**, 38050-71-4; **15b**, 22086-45-9; **15c**, 62015-69-4; 18, 78782-05-5; 10-undecenyl alcohol, 112-43-6; ethyl 10-undecanoate, 692-86-4; 10-undecenyl acetate, 112-19-6; 4-penten-1-ol, 821-09-0; 4-pentenyl methyl ether, 1191-31-7; 4-pentenyl chloride, 10524-08-0; 4-pentenyl acetate, 1576-85-8; allyl alcohol, 107-18-6; allyl chloride, 107-05-1; allyl methyl ether, 627-40-7; allyl acetate, 591-87-7; acrolein diethyl acetal, 3054-95-3; acrolein ethylene acetal, 3984-22-3; β-methyl allyl alcohol, 513-42-8; β-methylallyl chloride, 563-47-3; β-methyl allyl acetate, 820-71-3; methacrolein ethylene acetal, 20312-19-0; crotyl alcohol, 6117-91-5; crotyl chloride, 591-97-9; crotyl acetate, 628-08-0; crotyl methyl ether, 18408-99-6; crotyl ethyl ether, 18409-00-2; crotyl *tert*-butyl ether, 56121-50-7; crotyl tetrahydropyranyl ether, 4203-40-1; ethyl crotonate, 10544-63-5; *tert*-butyl crotonate, 3246-27-3; vinyl methyl ether, 107-25-5; vinyl acetate, 108-05-4; vinyl bromide, 593-60-2; ethyl acrylate, 140-88-5; isobutenyl chloride, 513-37-1; isobutenyl ethyl ether, 927-61-7; 1-chlorocyclopentene, 930-29-0; 1-ethoxycyclopentene, 17065-24-6; 1-acetoxycyclopentane, 933-05-1; 2-chloronorbornene, 694-93-9; 1,11-undecanediol, 765-04-8; ethyl 11-hydroxyundecanoate, 6149-49-1; 11-hydroxyundecylacetate, 78782-06-6; 1,5-pentanediol, 111-29-5; 5-methoxy-1-pentanol, 4799-62-6; 5-chloro-1-pentanol, 5259-98-3; 5-acetoxy-1-pentanol, 68750-23-2; 1,3-propanediol, 504-63-2; 3-chloro-1-propanol, 627-30-5; 3-methoxy-1-propanol, 1589-49-7; 3-acetoxy-1-propanol, 36678-05-4; 3,3-diethoxy-1-propanol, 16777-87-0; 2-(β-hydroxyethyl)-1,3-dioxolane, 5465-08-7; 2-methyl-1,3-propanediol, 2163-42-0; 2-methyl-3-chloropropanol, 10317-10-9; 2-methyl-3-acetoxypropanol, 55378-40-0; 2-(β-hydroxyisopropyl)-1,3-dioxolane, 78782-07-7; 1-butanol, 71-36-3; 1,2-butanediol, 584-03-2; 4-methoxy-2-butanol, 41223-27-2; 1-methoxy-2-butanol, 53778-73-7; 4-ethoxy-2-butanol, 53892-34-5; 1-ethoxy-2-butanol, 3448-32-6; 4-*tert*-butoxy-2-butanol, 1927-75-9; 1-*tert*-butoxy-2-butanol, 75567-10-1; crotyl *tert*-butyl ether, 56121-50-7; 4-OTHP-2-butanol, 78791-17-0; 1-OTHP-2-butanol, 78791-18-1; ethyl 2-ethyl-3-hexenoate, 78782-08-8; ethyl 2-ethyl-3-oxohexanoate, 5331-82-8; *tert*-butyl butyrate, 2308-38-5; 1-butene, 106-98-9; ethylene, 74-85-1; 2-methoxyethanol, 109-86-4; ethanol, 64-17-5; ethyl 3-hydroxypropionate, 623-72-3; 1,2-propanediol, 57-55-6; ethyl propionate, 105-37-3; isobutyl alcohol, 78-83-1; 1-ethoxy-2-methyl-2-propanol, 22665-68-5; cyclopentanol, 96-41-3; cyclopentanone, 120-92-3; 2-ethoxycyclopentanol, 78782-09-9; cyclopentene, 142-29-0; 1-acetoxycyclopentene, 933-06-2; 1,2-cyclopentanediol, 4065-92-3; *exo*-norbornanol, 497-37-0; 1,5-cyclooctanediol, 55343-44-7; 3-chloro-2-norbornanol, 4321-46-4; 9-BBN, 280-64-8; B-R-9-BBN (R = 2-chlorocyclopentanyl), 78782-10-2; B-OR-9-BBN (R = 2-chlorocyclopentanyl), 78782-11-3; B-R-9-BBN (R = 2-ethoxycyclopentanyl), 78782-12-4; B-OR-9-BBN (R = 2-ethoxycyclopentanyl), 78782-13-5; B-OR-9-BBN (R = 3-chloronorbornanyl), 78782-14-6.

Pyrolysis of *N,N*-Dihalo Derivatives of Amides and Sulfonamides[1]

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Pyrolysis of *N,N*-dichlorobenzenesulfonamide produced benzene (41%) and chlorobenzene (40%); the dibromo compound gave benzene (19%) and bromobenzene (20%). Toluene (46%), chlorotoluene (27%), and dichlorotoluene (10%) were generated from the *N,N*-dichloro-*p*-tolyl derivative. From each aryl substrate, 1,1,2,2-tetrachloroethane was also produced from reactions involving CH_2Cl_2 solvent. 3-Chloro-*N,N*-dichloroadamantane-1-sulfonamide decomposed to 1,3-dichloroadamantane (52%) and 1,3,5-trichloroadamantane (15%). *N,N*-Dihalobenzamides produced phenyl isocyanate; *N,N*-dichloro and *N*-bromo derivatives gave isocyanate in 16–23% and 21–28% yields, respectively. *N,N*-Dichloroadamantane-1-carboxamide produced 1-adamantyl isocyanate (20–50%) and 1-chloroadamantane (12–46%). The mechanistic features of the various reactions are discussed.

Pyrolyses of organic compounds containing a wide variety of functional groups have been rather extensively investigated.[2a] There are only small numbers of reports dealing with amines[2b,3] and their derivatives, e.g., amides,[4,5] sulfonamides,[6] and *N*-halo compounds.[1,7,8] Similarly, little attention has been devoted to *N*-halo derivatives of amides[4b] and sulfonamides.[9] Among the products from decomposition of chloramine B (*N*-sodio-*N*-chlorobenzenesulfonamide) were diphenyl sulfone, nitrogen, and sulfur dioxide.[10a] On being heated, *N*-chloro-*N*-*tert*-butyl-*n*-butanesulfonamide rearranged to give mainly *N*-*tert*-bu-

Table I. Thermolyses of *N,N*-Dihalo Sulfonamides[a]

substrate	products[b] (% yield)
$C_6H_5SO_2NCl_2$ [c]	C_6H_6 (41), C_6H_5Cl (40)
p-$CH_3C_6H_4SO_2NCl_2$ [d]	$C_6H_5CH_3$ (46), $ClC_6H_4CH_3$ (27),[e] $C_2H_6Cl_2$ (10)[e]
$C_6H_5SO_2NBr_2$ [f]	C_6H_6 (19), C_6H_5Br (20)
3-Cl-1-$AdSO_2NCl_2$ [g,h]	1,3-Cl_2Ad (52), 1,3,5-Cl_3Ad (15), Cl_4Ad (trace)

[a] Metal injector port. [b] 1,1,2,2-Tetrachloroethane was formed from the runs with aromatic substrates. [c] Solution (11% w/w) in CH_2Cl_2 at 425 °C. [d] Solution (17% w/w) in CH_2Cl_2 at 360 °C. [e] Isomer composition unknown. [f] Solution (5% w/w) in CH_2Cl_2 at 400 °C. [g] Solution (11% w/w) in CH_2Cl_2 at 355 °C. [h] Ad = adamantane.

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tyl-*n*-butanesulfonamide and *N*-*tert*-butyl-γ-chlorobutanesulfonamide, accompanied by some of the δ isomer (Hofmann–Löffler-type reaction).[10b] There is only one closely related prior reference, namely, decomposition of *N,N*-diiodobenzamide to phenyl isocyanate.[11]

Our aim was to determine the products from thermal decomposition of *N,N*-dihalo amides and sulfonamides and to address the reaction mechanisms.

Results and Discussion

The data from decomposition of *N,N*-dihalo sulfonamides in CH_2Cl_2 are summarized in Table I. With the aromatic dichloro types, approximately equal quantities (ca. 80% total yield) of parent hydrocarbon and halogenated derivative were formed. In the *p*-tolyl case, dichlorotoluene was also present according to the mass spectrum. Yields were lower with the *N,N*-dibromo substrate. In every experiment, the presence of 1,1,2,2-tetrachloroethane (8–11%) was detected and also possibly chloroform (<3%, based only on retention time, t_R, in GLC).

The aliphatic series was also examined. In an attempt to prepare 1-adamantanesulfonamide by modification of a literature procedure,[12] only 3-chloro-1-adamantanesulfonamide was isolated. Apparently, bridgehead chlorination is effected by $AlCl_3$–CCl_4 in accord with prior observations.[13-15] In contrast with the aromatic sulfonamides, the aliphatic substrate yielded mainly 1,3-dichloroadamantane, and some 1,3,5-trichloro derivative, but no 1-chloroadamantane or 1,1,2,2-tetrachloroethane.

For the aromatic compounds, on the basis of the products formed, it appears that the pyrolyses entail, at least in part, an intermolecular, free-radical mechanism (Scheme I). Aryl sulfonyl radicals (step d) are known to exist.[16]

Scheme I

$$C_6H_5SO_2NCl_2 \rightarrow C_6H_5SO_2\dot{N}Cl + [Cl\cdot] \quad (a)$$

$$C_6H_5SO_2NCl_2 \rightarrow C_6H_5SO_2\cdot + Cl_2N\cdot \quad (b)$$

$$C_6H_5SO_2\dot{N}Cl \rightarrow C_6H_5SO_2\cdot + NCl \quad (c)$$

$$C_6H_5SO_2\cdot \rightarrow C_6H_5\cdot + SO_2 \quad (d)$$

$$C_6H_5\cdot + CH_2Cl_2 \rightarrow C_6H_6 + Cl_2CH\cdot \quad (e)$$

$$C_6H_5\cdot + [Cl\cdot] \rightarrow C_6H_5Cl \quad (f)$$

$$2Cl_2CH\cdot \rightarrow Cl_2CHCHCl_2 \quad (g)$$

$$Cl_2CH\cdot + [Cl\cdot] \rightarrow Cl_3CH \quad (h)$$

$$2NCl \rightarrow ClN{=}NCl \rightarrow N_2 + Cl_2 \quad (i)$$

Step d has a counterpart entailing an aliphatic sulfonyl radical.[17] Analogy for the dimerization in step g is found in the formation of $CH_3CCl_2CCl_2CH_3$ from 1,1-dichloroethane and acetyl peroxide.[18] The source of [Cl·] in steps f and h might be (1) $C_6H_5SO_2NCl_2$, (2) Cl_2N_2, (3) $Cl_2N\cdot$, or (4) Cl_2. In relation to step i, since chloronitrene is highly energetic, it may well attack another component in the system before dimerization can take place.

Table II. Pyrolyses of *N*-Halo Amides

substrate	product (% yield)
$C_6H_5CONCl_2$ [a]	C_6H_5NCO (16-23) [b]
1-$AdCONCl_2$ [c]	1-AdNCO (19-37), 1-AdCl (12-46)

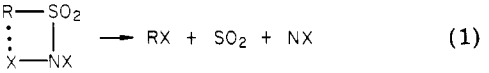
[a] Metal injector; temperature 250 °C; neat or solution (11% or 21% w/w) in CH_2Cl_2. [b] Small amounts (<5%) of chlorophenyl isocyanate were noted from neat injection. [c] Metal injector; temperature 195-395 °C; 9% (w/w) solution in CH_2Cl_2; Ad = adamantyl.

Experimental support for intermolecularity in the pathway leading to aromatic hydrocarbon product was obtained. When the reaction with $C_6H_5SO_2NCl_2$ was carried out with cumene as the hydrogen donor, the ratio of C_6H_6 to C_6H_5Cl increased to 2:1. The total yield (66%) decreased somewhat. In addition, nine other products (unidentified) were present according to GLC. In bromotrichloromethane solution (7% w/w), chlorobenzene (27%) and bromobenzene (50%) were formed. The bromobenzene apparently arises via bromine atom abstraction from $BrCCl_3$ by phenyl radical. A control experiment revealed that $BrCCl_3$ decomposed to at least seven products at 400 °C. On the other hand, there were no indications of intermolecular radical reactions for 3-chloro-1-adamantanesulfonamide. Neither 1-chloroadamantane nor 1,1,2,2-tetrachloroethane was detected.

Evidence that CH_2Cl_2 does not act as a chlorine atom donor to phenyl radicals was obtained from thermolysis of benzoyl peroxide in CH_2Cl_2. The observed products were benzene, biphenyl, and 1,1,2,2-tetrachloroethane but no chlorobenzene. Decomposition of *N,N*-dibromobenzenesulfonamide in CH_2Cl_2 yielded no chlorobenzene, providing added support for the view that only hydrogen abstraction from solvent occurs.

The lower product yield from the *N,N*-dibromo substrate indicates participation of one or more undetected pathways. The weaker N–Br bond vs. the N–Cl bond may lead to α elimination of bromine with formation of benzenesulfonyl nitrene. This reactive intermediate is reported for the gas-phase thermolysis of benzenesulfonyl azide, which produced mainly sulfur dioxide and azobenzene, together with small amounts of biphenyl, diphenylamine, and benzenesulfonamide.[19] However, any aniline derivatives or benzenesulfonamide generated in our system would not be amenable to GLC analysis.

Formation of aryl halide and 1,3-dichloroadamantane can be rationalized by an intramolecular mechanism (eq 1). Although homolysis cannot be ruled out, analogy with



(1)

R = aryl, alkyl

prior, related systems suggests ion-pair participation by an S_Ni mechanism. This type of route involving a four-membered transition state was advanced for aryl fluoroformates,[20] alkyl chloroformates,[2a] and alkyl chlorosulfites.[21a] Similar three-membered transition states may exist during the conversion of RNX_2[7] and RSO_2Cl[22] to

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alkyl halides. 1,3,5-Trichloroadamantane likely arises from subsequent chlorination of the 1,3-dichloro derivative. *N*-Halo compounds are known to effect bridgehead halogenation of 1-chloroadamantane.[7]

Thermal reactions of *N,N*-dichloro carboxamides of benzene and adamantane were also investigated. The findings are summarized in Table II. Phenyl isocyanate, isolated in rather low yield, was the principal product identified from *N,N*-dichlorobenzamide. Also present was a small amount of a chlorophenyl isocyanate, on the basis of mass spectral analysis: molecular ions at *m/e* 153 (isotopic cluster) with the base peak at *m/e* 119 (phenyl isocyanate). A few reaction variables were examined. Altering the concentration of the *N,N*-dichloro compound, from 11% w/w to neat, produced little change in yield.

Thermolysis of the *N,N*-dichloro amide from adamantane produced 1-adamantyl isocyanate (20–40% yield) and 1-chloroadamantane (10–45% yield). A study of the temperature parameter in the 195–395 °C reaction (9% w/w in CH_2Cl_2) indicated a relatively constant yield (ca. 33%) of isocyanate over the range. In contrast, the amount of bridgehead chloride increased from 15% to 46% with the temperature increase. With a more dilute solution (3.5 w/w) at 325 °C, the yield of isocyanate rose from 38% to 48%, accompanied by a decrease for chloride from 32% down to 27%.

Mechanistically, it appears that isocyanate formation occurs via ionic or concerted pathways. One possibility is presented in Scheme II. After the starting material

Scheme II

$$\text{RCONXY} \xrightarrow{-X^+} \text{RCONY}^- \xrightarrow{-Y^-} \text{RNCO}$$

R = aryl, alkyl; X = Cl, H; Y = Cl, Br

serves as a source of chlorine in the +1 state, rearrangement takes place with loss of halide ion. This postulate resembles the generally accepted concerted pathway for the Hofmann (Y = Br, Cl), Lossen (Y = OH), and Curtius[23] (Y = N_2) rearrangements.[21b]

Alternatively, α elimination of XY would produce a nitrene intermediate which then undergoes rearrangement to the end product (Scheme III). This type of scheme was advanced by Gottardi to account for the conversion of *N,N*-diiodobenzamide to phenyl isocyanate.[11]

Scheme III

$$\text{RCONXY} \xrightarrow{-XY} \text{RCON} \rightarrow \text{RNCO}$$

Furthermore, a homolytic mechanism is unlikely on the basis of the absence of products expected from such processes. For example, there was no evidence for benzene, benzamide, or 1,1,2,2-tetrachloroethane in the decomposition of *N,N*-dichlorobenzamide (CH_2Cl_2). Photolysis of *N*-chlorobenzamide in benzene generated benzamide as the major product,[24] apparently via homolytic cleavage of the N–Cl bond. It is mechanistically significant (see the discussion on the isocyanate product) that biphenyl was also formed, but only a very small amount of isocyanate and no chlorobenzene.

Formation of the bridgehead chloride of adamantane must proceed by a route which entails overall loss of ClNCO. A reasonable pathway is shown in Scheme IV.

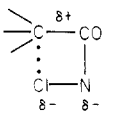
Scheme IV

$$\text{1-AdCONCl}_2 \xrightarrow{-Cl^+} \text{1-AdCONCl}^- \xrightarrow{-NCO} \text{1-AdCl}$$

The mechanistic detail apparently is closely related to that for the rearrangement of N-bromo-α-halo amides to *gem*-dihalides under Hofmann degradation condtions[25,26] (eq 2). On the basis of supporting evidence, Stevens and

$$R_2CClCONBr^- \rightarrow R_2CClBr + NCO^- \qquad (2)$$

coworkers proposed an intramolecular, stereospecific, four-center mechanism.[25] The driving force may consist of attack on the α-carbon by nucleophilic bromine or incipient formation of cyanate ion.[26] In this scheme, the α-carbon displays cationic character. It is pertinent that the solvolytic rate for R_2CXCl (X = leaving group) is accelerated by the chlorine substituent directly bonded to the carbonium ion intermediate.[27] Thus, resonance predominates over the inductive effect, resulting in stabilization of the carbocation. When this idea is applied to our system, one can then visualize the transition state as in 1. On the basis of the ability of the α-carbon to become



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electron deficient, it is reasonable that 1-AdCONCl_2 generates chloride product, in contrast with the behavior of $C_6H_5CONCl_2$.

Experimental Section

Dichloromethane was purified by being dried over $CaCl_2$ and fractionally distilled from CaH and was stored in amber bottles over molecular sieves (4 Å).[28a]

***N,N*-Dichlorobenzenesulfonamide.** Use of a prior procedure[29] yielded 9.8 g (89% yield) of material: mp 69.5–73.5 °C (lit.[30] mp 72–76 °C); $[Cl^+]$ = 100%; ^1H NMR ($CDCl_3$) δ 8.3–7.6 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 135.44 (C-1), 131.34 (C-2,6), 129.11 (C-3,4,5).

***N,N*-Dibromobenzenesulfonamide.** A 95% yield of product was obtained by a modified literature method[31] (2 equiv of brominating agent): mp 71–111 °C; $[Cl^+]$ = 101%; ^1H NMR ($CDCl_3$) δ 8.4–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 136.04 (s, C-1), 131.54 (d, C-2,6), 129.29 (d, C-3,4,5).

***N,N*-Dichloro-4-toluenesulfonamide.** A previous method[29] gave a 60% yield of tan crystals: mp 74–86 °C (lit.[32] mp 78–84 °C); $[Cl^+]$ = 99%; ^1H NMR ($CDCl_3$) δ 8.0 (d, 2 H), 7.4 (d, 2 H), 2.5 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 149.75 (s, C-1), 131.64, 129.98 (d, C-2,3,5,6) 125.98 (s, C-4) 22.59 (q, C-4).

3-Chloro-1-sulfonamidoadamantane. This compound was isolated in 10% yield according to a modified literature procedure:[12] the reaction mixture was stirred with CCl_4–$AlCl_3$ for 3 h at room temperature, rather than at 0 °C: mp 154–156 °C; ^1H NMR ($CDCl_3$) δ 7.25 (s, 2 H), 2.4 (s, 4 H), 2.2–2.0 (m, 8 H), 1.7 (m, 2 H); IR (Nujol) 3400, 3300 (NH) cm^{-1}.

Anal. Calcd for $C_{10}H_{16}ClNO_2S$: C, 48.29; H, 6.48; N, 5.63. Found: C, 48,14; H, 6.74; N, 5.43.

1-(*N,N*-Dichlorosulfonamido)-3-chloroadamantane. 3-Chloro-1-sulfonamidoadamantane (0.6 g) was dissolved in CH_2Cl_2 (20 mL), cooled to 0 °C by an ice bath, and protected from light by aluminum foil. *tert*-Butyl hypochlorite[33] (2.0 g), prepared via

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a literature procedure and used without purification, was added. The reaction mixture was stirred for 2 h with cooling. Removal of the solvent by flash evaporation yielded the desired product as a white solid: 0.8 g (100%); mp 62.5–73 °C dec; [Cl⁺] = 100%; ^{1}H NMR ($CDCl_3$) δ 2.6 (s, 2 H), 2.5–2.0 (m, 10 H), 1.7 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 70.00 (s, C-1), 65.03 (s, C-3), 46.18 (t, C-2), 45.68, 35.73, 33.59, 31.25 (C-4-10).

Pyrolysis of Sulfonamide Derivatives. General Procedure. Injection of 10 μL (20–35% w/w) of 1-(*N,N*-dichlorosulfonamido)-3-chloroadamantane in CH_2Cl_2 into the GLC (15% SE-30 on Chromosorb W, stainless-steel column, 7 ft × $^1/_4$ in.; metal injector port; temperature 350 °C; column temperature 170 °C; He flow rate 60 mL/min) gave five peaks: (1) *m/e* 205, (2) *m/e* 240, (3–5) *m/e* 276. Peaks 1 and 2 were identified by retention time, peak enhancement, and mass spectral comparison with authentic materials. Isotopic clusters of chlorine in the mass spectrum were used in the identification of peaks 3–5; however, the structures of the individual isomers were not ascertained.

Purification of Cumene. A literature[28b] procedure gave pure material by fractional distillation; bp 151–152 °C (754 torr).

***N,N*-Dichlorobenzamide.** Undistilled *tert*-butyl hypochlorite[33] (13 g, 0.12 mol) was cooled in CH_2Cl_2 (50 mL) to 0 °C with an ice bath in the absence of light and moisture. Benzamide (7 g, 0.06 mol) in cold CH_2Cl_2 (75 mL) was added in one portion. The resulting solution was stirred for 2 h at 0 °C and for 1 h at room temperature. Concentration on the rotary evaporator yielded a dark green oil: 9.1 g (0.048 mol, 80%); [Cl⁺] = 99%; ^{1}H ($CDCl_3$) δ 8.3–7.6 (m, 5 H).

1-Adamantanecarboxamide. Adamantane-1-carbonyl chloride (6.6 g, 0.037 mol) in dry dioxane (40 mL) was added dropwise to concentrated ammonium hydroxide solution (150 mL). Filtration yielded 3.5 g of off-white solid, mp 184–191 °C. Concentration of the mother liquor provided an additional 1.1 g of solid. Recrystallization (dry hexane) gave a white powder: 4.1 g (62%); mp 187.5–190 °C (lit.[34] mp 189 °C); ^{1}H NMR ($CDCl_3$) δ 2.3–1.7 (m, 15 H), 1.1 (s, 2 H); IR ($CDCl_3$) 3650, 1720, 1630 cm^{-1}.

***N,N*-Dichloro-1-adamantanecarboxamide.** A prior procedure[29] gave a viscous, odorless, yellow oil, which was dissolved in petroleum ether (bp 30–60 °C) and filtered to remove 0.35 g of solid ([Cl⁺] = 50%). Concentration of the filtrate yielded a yellow-green oil which immediately turned to a light yellow solid: 5 g (0.020 mol, 71%), [Cl⁺] = 97–98%; mp 36.5–40 °C. Recrystallization (Skelly B) yielded light green crystals: mp 38–38.5 °C (sinster at 37 °C); [Cl⁺] = 99%; ^{1}H NMR ($CDCl_3$) δ 2.2–2.0 (s, 8 H), 2.0–1.7 (s, 7 H); IR ($CDCl_3$) 1750, 1470, 1350, 1010 cm^{-1}.

Anal. Calcd for $C_{11}H_{15}Cl_2NO$: C, 53.24; H, 6.09; N, 5.64. Found: C, 54.03; H, 6.51; N, 5.69.

1-Adamantyl Isocyanate. The method of Stetter and Wulff[35] was used to obtain material [mp 141–143 °C (lit.[34] mp 144–145 °C)] which was found to contain a small amount of 1-bromoadamantane: ^{1}H NMR ($CDCl_3$) δ 2.6–1.6, (m, 11 H), 1.0 (s, 4 H); mass spectrum, *m/e* (relative intensity) 215 (3), 177 (8), 135 (100), 134 (11), 121 (12), 120 (86), 119 (4); IR ($CDCl_3$) 2225 (w) cm^{-1}.

Pyrolysis of Carboxamide Derivatives. General Procedure. Injection of 10 μL of a solution (11.4% w/w) of *N,N*-dichlorobenzamide in CH_2Cl_2 into the gas–liquid chromatograph (30% SE-30 on Chromosorb W; copper column, 8 ft × $^1/_4$ in.; metal injector; temperature 250 °C; column temperature 110 °C; He flow rate 90 mL/min) gave one major peak in addition to peaks due to air and solvent. Phenyl isocyanate was identified by comparison of retention times, peak enhancement (GLC), mass spectrum, and IR spectrum with those of authentic material. Injection of 30 μL of neat *N,N*-dichlorobenzamide yielded predominantly phenyl isocyanate. However, three other smaller peaks were detected with the following molecular ions: (2) *m/e* 103, (3) *m/e* 140, (4) *m/e* 155. The isotopic cluster for chlorine showed no. 4 to be a chlorinated phenyl isocyanate.

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Registry No. *N,N*-Dichlorobenzenesulfonamide, 473-29-0; *N,N*-dibromobenzenesulfonamide, 938-05-6; *N,N*-dichloro-4-toluenesulfonamide, 473-34-7; 3-chloro-1-sulfonamidoadamantane, 78610-03-4; 1-(*N,N*-dichlorosulfonamido)-3-chloroadamantane, 78610-04-5; *N,N*-dichlorobenzamide, 22180-78-5; 1-adamantanecarboxamide, 5511-18-2; adamantane-1-carbonyl chloride, 2094-72-6; *N,N*-dichloro-1-adamantanecarboxamide, 78624-42-7.

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Intermediates in the Peroxy Acid Oxidation of Phenyl Phenylmethanethiosulfinate[1,2]

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The *m*-chloroperoxybenzoic acid (MCPBA) oxidation of phenyl phenylmethanethiosulfinate (**9**) in $CDCl_3$ has been studied. Low-temperature ^{1}H NMR and ^{13}C NMR spectra show that phenyl phenylmethanethiosulfonate (**7**), phenylmethanesulfonic acid (**26**), and phenylmethanesulfinic acid (**27**) are formed during the early stages of oxidation. Although **7** may be formed via direct attack of MCPBA at the sulfinyl sulfur atom of **9**, the presence of **7**, **26**, and **27** is also explicable in terms of formation and rearrangement of metastable α-disulfoxide (**13**) and sulfenyl sulfinate (**14**) intermediates.

The formation of α-disulfoxides (**3**) and sulfenyl sulfinates (**4**) as intermediates in the oxidation of disulfides (**1**) or thiosulfinates (**2**) to thiosulfonates (**5**) has been suggested for in vivo[3,4] and in vitro[4-17] reactions (Scheme I). Attempts to prepare these long-sought elusive interme-

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