Figure 2. Illustration of the hyperconjugative interaction present in (a) allyl cation and (b) allyl chloride which increases the electron density on chlorine.

The resonance interaction between C=C and C^+ that stabilizes the allyl cation (Figure 2a) is also present in allyl chloride, in the form of a hyperconjugative interaction between the C=C π bond and the C–Cl σ bond (Figure 2b).[9f] A semiquantitative estimation of the amount of hyperconjugation due to the C–Cl bond in allyl chloride has been made by Schweig et al.[9f] In this estimation the C–Cl bond is found to have a hyperconjugative effect about equivalent to that of the C–H bond. If one considers an analogous treatment of our 2,3-dichloropropene/2-chloropropene/vinyl chloride system, the hyperconjugative effect of the C–Cl bond is found to be almost 1.5 times that of the C–H bond. We believe this relationship to be very reasonable especially since in our system more hyperconjugation should be possible due to the conjugative interaction of the vinyl chloride. This hyperconjugative interaction results in a transfer of negative charge to chlorine which manifests itself by a decrease in the lone-pair ionization potential of chlorine[9] and by a decrease in the ^{35}Cl nuclear quadrupole resonance frequencies.[10,11]

Since conjugative interactions between Cl and the double bond in a vinyl chloride lead to a positive charge on chlorine and so to an increase in the lone-pair ionization potential, the second ionization potential of a chlorinated allyl chloride should correspond to ionization of a lone pair of the allylic chlorine. Removal by the precolumn would then be expected to occur only for compounds whose second ionization potentials lie below some critical value.

Table III shows calculated (MNDO) and observed (PES) second ionization potentials for the compounds studied here. It will be seen that they do indeed correspond to the predicted pattern. All chlorides with a second ionization potential below 11.35 eV (observed) or 12.32 eV (calculated) were removed by the column but none with values above these limits.

Use of nuclear quadrupole resonance (NQR) data is less direct in this connection because the conjugative interactions in vinyl chlorides also lower the ^{35}Cl NQR frequencies. Moreover, data are available for only two of the allyl chlorides in Table I, i.e., III (34.69 MHz[10]) and VI (34.11 MHz[11]). However, these are consistent with our interpretation, VI being removed by the precolumn whereas III was not. On this basis one would expect the precolumn also to remove benzyl chloride (33.63 MHz[11]) even though it is not an olefin derivative.

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Registry No. 1, 557-98-2; I, 563-47-3; II, 21400-25-9; III, 78-88-6; IV, 75-35-4; *cis*-V, 10075-38-4; *trans*-V, 7415-31-8; *cis*-VI, 1476-11-5; *trans*-VI, 110-57-6; VII, 760-23-6; VIII, 156-60-5; IX, 156-59-2; tetrachloroethene, 127-18-4; 3-chloro-2-(chloromethyl)-1-propene, 1871-57-4; trichloroethene, 79-01-6; *cis*-1,3-dichloro-1-propene, 10061-01-5; 3-chloro-1-propene, 107-05-1; chloroethene, 75-01-4; mercuric sulfate, 7783-35-9.

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Efficient Peroxyoxalate Chemiluminescence from Reactions of *N*-(Trifluoromethylsulfonyl)oxamides with Hydrogen Peroxide and Fluorescers[1]

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Chemilumescence quantum yields above 0.11 einstein mol^{-1} (11%) were obtained from six *N*-(trifluoromethylsulfonyl)oxamides substituted on nitrogen by electronegatively substituted aryl groups. One compound, *N,N'*-bis(trifluoromethylsulfonyl)-*N,N'*-bis(2,4,5-trichlorophenyl)oxamide, provided a chemiluminescent quantum yield of 34%, making it the most efficient nonenzymatic compound known. Molecular sieves were found to be effective catalysts for the preparation of certain trifluoromethylsulfonamides from the amine and trifluoromethylsulfonyl chloride and for the preparation of the oxamides from oxalyl chloride and sulfonamide.

Peroxyoxalate chemiluminescence[2] is illustrated by the reaction sequence outlined in Scheme I.

Chemiluminescence quantum yields of 0.10 to 0.18 einstein mol^{-1} (10–18%) have been reported for the oxalic ester A with fluorescers such as 9,10-bis(phenylethynyl)-anthracene (green) and 1-chloro-9,10-bis(phenylethynyl)-anthracene (yellow).[3,4] Other oxalic esters such as bis(2,-4,6-trichlorophenyl) oxalate,[5,6] bis(2,4-dinitrophenyl) oxa-

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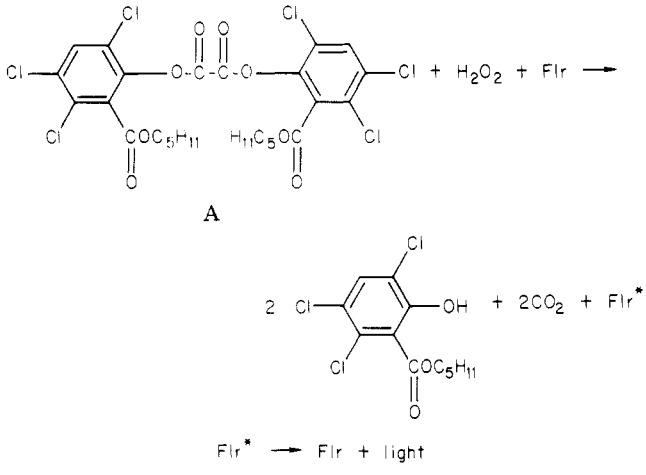
Table I. Chemiluminescence Performance of *N*-Trifyloxamides,[a] $F_3CO_2SN(R)COCON(R)SO_2CF_3$

compd no.	concn, M	QY,[b] $\times 10^{-2}$	mean QY	$T(75)$,[c] min	light capacity[d]
1, R = 4-chlorophenyl	0.01	11.4		44.9	37.5
2, R = 2,4-dichlorophenyl	0.01	26.2		139.00	85.0
	0.01	25.6	25.9	116.00	85.4
3, R = 2,4,5-trichlorophenyl	0.01	32.6		50.4	108
	0.01	35.4	34.0	42.3	117
4, R = 2,4,6-trichlorophenyl	0.01	11.4		100	37.8
	0.01	13.6	12.5	82.9	45.0
5, R = 4-nitrophenyl	0.01	11.0		8.88	35.7
6, R = 2-methoxyethyl	0.01	2.85		70.2	9.20
7, R = 2-chloroethyl	0.01	3.68		125	12.2
8, R = 2-chloro-3-pyridyl	0.008	15.5		129	41.3

[a] Chemiluminescent reactions contained the indicated concentrations of the oxamide, 6.75×10^{-3} M 1-chloro-9,10-bis(phenylethynyl)anthracene, 0.375 M hydrogen peroxide, and 3×10^{-4} M sodium salicylate, in a solvent mixture of 75% (by volume) dibutyl phthalate, 20% dimethyl phthalate, 5% *tert*-butyl alcohol. [b] Chemiluminescent quantum yield (QY) in einsteins per mole of oxamide. [c] Time required for 75% of the total light to be emitted. [d] Integrated visible light output in lumen-hours per liter.

Scheme I



Flr = a fluorescent compound

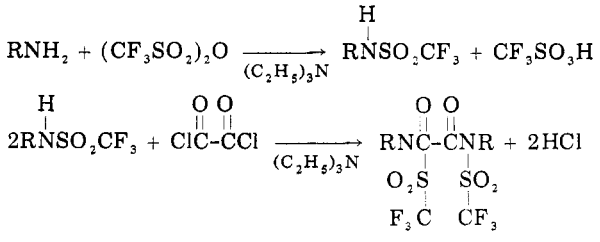
late[5,7] and bis(3-(trifluoromethyl)-4-nitrophenyl) oxalate[5] have provided chemiluminescence quantum yields as high as 22 to 27%.

Other oxalic acid derivatives including mixed anhydrides,[8] amides,[8] sulfonamides,[9] and oxalyl chloride[10] also provide chemiluminescence from this reaction but are less efficient. In general, efficient peroxyoxalate chemiluminescence requires an oxalic acid derivative with an easily displaced leaving group.[2] In general, leaving groups containing electron-attracting substituents have provided the highest efficiencies.

Results and Discussion

Inasmuch as the trifluoromethylsulfonyl (trifyl) group is one of the most powerful electron-withdrawing groups known,[11] we have investigated the chemiluminescence efficiency of a series of *N*-trifyloxamides in the peroxyoxalate chemiluminescent system. The results, summarized in Table I, indicate that *N*-trifyloxamides which are further substituted on nitrogen by electronegatively substituted aromatic groups provide high chemiluminescence efficiency. Indeed, the 2,4,5-trichloro compound **3** proved to be the most efficient nonenzymatic chemiluminescent compound yet discovered, with a chemiluminescent quantum yield of 34%.

Scheme II. Synthesis of *N*-Trifyloxamides



The data in Table I indicate that increasing chlorine substitution on the aromatic ring of diphenyltrifyloxamide generally provides a concurrent increase in chemiluminescence efficiency. However, the 2,4,6-trichloro derivative **4** was substantially less efficient than the 2,4,5-trichloro derivative **3**, even though an ortho substituted chlorine is more electronegative than a meta.[12] As expected, substitution of aliphatic groups on the nitrogens of *N*-trifyloxamide resulted in substantially reduced efficiency.

The general method for preparation of the trifyloxamides involved treatment of the amine with triflic anhydride at low temperature following procedures similar to those described by Hendrickson and Bergenson.[13] The acidic trifylamides were then acylated with oxalyl chloride in the presence of triethylamine to yield the desired trifyloxamides (Scheme II).

The presence of a labile chlorine atom in *N*-(2-chloroethyl)trifluoromethylsulfonamide negated the use of triethylamine as the acid acceptor. In this case, powdered 3A molecular sieves[14] effectively catalyzed the sulfonamide formation, while the use of "Proton Sponge", 1,8-bis(dimethylamino)naphthalene, a strong proton acceptor but a poor nucleophile,[15] prevented the displacement of the chlorine in the reaction of the trifylamide with oxalyl

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chloride and afforded the oxamide in 80% crude yield. Molecular sieves were also effective catalysts for both the trifylamide formation and the preparation of the oxamide 8. Trifylamides N-(4-chlorophenyl)trifluoromethylsulfonamide (**1a**), N-(2,4-dichlorophenyl)trifluoromethylsulfonamide (**2a**), N-(2,4,5-trichlorophenyl)trifluoromethylsulfonamide (**3a**), and N-(4-nitrophenyl)trifluoromethylsulfonamide (**5a**) have been reported previously.[16]

Experimental Section

Melting points were taken on a "Mel-Temp" block and are uncorrected. IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer; samples were run in Nujol or in methylene chloride solutions. NMR spectra were recorded on a Varian Associates Model EM 360A spectrometer, using tetramethylsilane as an internal standard. Mass spectra were recorded on a VG Micromass Model 7070F high-resolution mass spectrometer attached to a VG Model 2035 data system, using the electron impact (EI) mode or the chemical ionization (CI) mode. In the CI mode, methane was used as the reagent gas. Microanalyses were performed by the Micro Analytical Laboratories of American Cyanamid Company, Bound Brook, N.J.

Determination of Chemiluminescence Quantum Yields. Absolute light measurements were made on a spectroradiometer-luminometer similar to that described by Roberts and Hirt[17] modified with a Janell-Ash Model 82-410 grating monochromator and an RCA C31034 photomultiplier with a gallium arsenide photocathode operated at 1300 V with dry ice cooling. Raw data were recorded digitally on a Hewlett-Packard 5150A thermal printer. Spectral response was corrected by calibration against a standard tungsten lamp. Absolute light intensities were obtained by deriving calibration constants based on the accepted fluorescence quantum yield (0.55) for quinine sulfate [18] in 0.1 N H_2SO_4 and by ferrioxalate actinometry[19] of the exciting light. Chemiluminescence quantum yields in einsteins per mole of oxamides were calculated by monitoring the intensity decay at a single wavelength and calculating the intensity at each time interval in einsteins per second from the chemiluminescence spectrum. Chemiluminescence spectra were corrected for intensity decay. The total area under the decay curve was calculated by using a combination of a Simpson's rule integration and an exponential extrapolation to infinite time.[17] Data were processed via a Digital Equipment Corp. PDP-1140 computer.

***N*-(4-Chlorophenyl)trifluoromethylsulfonamide (1a).** To a solution of 4-chloroaniline (5.12 g; 0.04 mol) and triethylamine (4.04 g; 0.04 mol) in 60 mL of methylene chloride was added in portions 6.73 mL (0.04 mol) of trifluoromethanesulfonic anhydride at 0 °C under a nitrogen atmosphere. The mixture was stirred at room temperature for 4 h. Evaporation of the solvent gave 10.2 g of light brown oil, which solidified upon standing at room temperature. Recrystallization of the solid from cyclohexane gave 9.6 g (93%) of pure **1a**: mp 45–47 °C; IR (CH_2Cl_2) 3300, 1360, 1200, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.2 (s, 1 NH) and 7.3 to 7.4 (2 s, 4 aromatic protons); mass spectrum (EI), *m/e* 259 (M^+). Anal. Calcd for $C_7H_5NO_2SClF_3$: C, 32.43; H, 1.93; N, 5.41; S, 12.36; Cl, 13.51; F, 22.06. Found: C, 32.49; H, 1.80; N, 5.55;, S, 12.21; Cl, 13.30; F, 21.79.

***N*,*N*′-Bis(4-chlorophenyl)-*N*,*N*′-bis(trifluoromethylsulfonyl)oxamide (1).** Oxalyl chloride (0.5 mL; 0.056 mol) was added dropwise to a stirred solution of **1a** (2.6 g; 0.01 mol) and triethylamine (1.0 g; 0.01 mol) in 20 mL of 1,2-dimethoxyethane at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 2 h, heated to 60 °C, held at 60 °C for 1 h, and evaporated to obtain a yellow solid which was treated with 20 mL of water. The solid which remained after the water extraction was collected and recrystallized from anhydrous ether to give 2.46 g (85%) of white crystalline **1**: mp 173–174 °C; IR (Nujol) 1750, 1730, 1210, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.30 to 7.65 (m, aromatic protons); mass spectrum (EI), *m/e* 572 (M^+). Anal. Calcd for $C_{16}H_8N_2O_6S_2Cl_2F_6$: C, 33.50; H, 1.40; N, 4.88; S, 11.17; Cl, 12.40; F, 19.90. Found: C, 33.51, H, 1.38; N, 4.74; S, 11.52; Cl, 12.10; F, 19.61.

***N*,*N*′-Bis(2,4-dichlorophenyl)-*N*,*N*′-bis(trifluoromethylsulfonyl)oxamide (2).** The trifylamide **2a** was prepared by the procedure described for **1a** using anhydrous ether as solvent affording 97% of crude product which after recrystallization from cyclohexane gave pure **2a**: mp 84–86 °C; IR (Nujol) 3250, 1360, 1200, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.21 (s, 1 NH) and 7.3 to 7.7 (m, 3 aromatic protons); mass spectrum (EI), *m/e* 293 (M^+). Anal. Calcd for $C_7H_4NO_2SCl_2F_3$: C, 28.67; H, 1.37; N, 4.78; S, 10.88; Cl, 23.89; F, 19.39. Found: C, 28.55; H, 1.44; N, 4.85; S, 11.15; Cl, 24.00; F, 18.95.

Trifylamide **2a** was converted to the oxamide **2** according to the procedure described for **1**. Recrystallization from cyclohexane afforded pure **2** (yield, 94%): mp 148–150 °C; IR (CH_2Cl_2) 1750, 1730, 1210, and 1130 cm^{-1}; NMR (acetone-d_6) δ 7.7 and 7.9 (aromatic protons); mass spectrum (EI), *m/e* 642 (M^+). Anal. Calcd for $C_{16}H_6N_2O_6S_2Cl_4F_6$: C, 29.92; H, 0.90; N, 4.36; S, 10.00; Cl, 22.12; F, 17.75. Found: C, 30.24; H, 1.02; N, 4.24; S, 10.45; Cl, 22.27; F, 17.19.

***N*,*N*′-Bis(2,4,5-trichlorophenyl)-*N*,*N*′-bis(trifluoromethylsulfonyl)oxamide (3).** The trifylamide **3a** was prepared according to the procedure described for **1a**. Recrystallization of the crude product from cyclohexane afforded pure **3a** (yield, 82%): mp 104–106 °C; IR(CH_2Cl_2) 3300, 1360, 1210, and 1140 cm^{-1}; NMR ($CDCl_3$) 6.4 (s, 1 NH), 7.6 and 7.8 (2s, 2 aromatic protons); mass spectrum (EI), *m/e* 327 (M^+). Anal. Calcd for $C_7H_3NO_2SCl_3F_3$: C, 25.69; H, 0.92; N, 4.28; S, 9.79; Cl, 32.11; F, 17.43. Found: C, 25.59; H, 1.00, N, 4.35; S, 9.95; Cl, 31.98; F, 17.00.

The oxamide **3** was prepared from **3a** according to the method already described for **1**, using methylene chloride as solvent. Recrystallization from methylcyclohexane afforded pure **3** (yield, 78%): mp 190–192 °C; IR (CH_2Cl_2) 1750, 1730, 1340, 1210, and 1120 cm^{-1}; NMR (acetone-d_6) δ 7.7 and 7.9 (2 s, aromatic protons); mass spectrum (EI), *m/e* 708 (M^+). Anal. Calcd for $C_{16}H_4N_2O_6S_2Cl_6F_6$: C, 27.02; H, 0.57; N, 3.94; S, 9.02; Cl, 29.91; F, 16.04. Found: C, 27.02; H, 0.63; N, 3.84; S, 8.90; Cl, 30.06; F, 16.64.

***N*,*N*′-Bis(2,4,6-trichlorophenyl)-*N*,*N*′-bis(trifluoromethylsulfonyl)oxamide (4).** Trifylamide **4a** was prepared by the procedure already described for **1a**. Vacuum sublimation of the crude product afforded pure **4a** (yield, 91%): mp 99–101 °C; IR (CH_2Cl_2) 3300, 1360, and 1160 cm^{-1}; NMR ($CDCl_3$) δ 6.5 (s, 1 NH) and 7.8 (s, 2 H, 2 aromatic protons); mass spectrum (EI), *m/e* 327 (M^+). Anal. Calcd for $C_7H_3NO_2SCl_3F_3$: C, 25.69; H, 0.92; N, 4.28; S, 9.79; Cl, 32.11; F, 17.43. Found: C, 25.52; H, 0.98; N, 4.40; S, 10.01; Cl, 32.15; F, 17.31.

Trifylamide **4a** was converted to the oxamide **4** by the procedure described for **1**. Recrystallization from cyclohexane afforded pure **4** (yield, 73%): mp 170–172 °C; IR ($CDCl_3$) 1740, 1380, 1260, 1210, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.8 (s, aromatic protons); mass spectrum (EI), *m/e* 708 (M^+). Anal. Calcd for $C_{16}H_4N_2O_6S_2Cl_6F_6$: C, 27.02; H, 0.57; N, 3.94; S, 9.02; Cl, 29.91; F, 16.04. Found: C, 26.91; H, 0.60; N, 3.80; S, 8.85; Cl, 30.02; F, 16.40.

***N*,*N*′-Bis(4-nitrophenyl)-*N*,*N*′-bis(trifluoromethylsulfonyl)oxamide (5).** The crude trifylamide **5a** (yield, 72%) was prepared by the procedure described for **1a**: IR (CH_2Cl_2) 3250, 1350, 1220, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.3 (s, 1 NH) and 7.4 to 7.5 (2 s, 4 aromatic protons); mass spectrum (EI), *m/e* 270 (M^+). It was used without further purification in the preparation of the oxamide **5**, following the procedure already described for **1**. Recrystallization from diethyl ether afforded pure **5** (yield, 92%): mp 172–175 °C; IR (CH_2Cl_2) 1750, 1730, 1350, 1210, and 1130 cm^{-1}; NMR ($CDCl_3$) δ 7.7 to 7.9 (4 s, aromatic protons); mass spectrum (EI), *m/e* 562 (M^+). Anal. Calcd for $C_{16}H_8N_4O_8S_2F_6$: C, 34.16; H, 1.42; N, 9.96; S, 11.39; F, 20.28. Found: C, 34.46; H, 1.25; N, 9.80; S, 11.78; F, 19.82.

***N*,*N*′-Bis(2-methoxyethyl)-*N*,*N*′-bis(trifluoromethylsulfonyl)oxamide (6).** The trifylamide **6a** (yield, 96%) was prepared by the procedure described for **1a**. Vacuum distillation afforded pure **6a**: bp 50–51 °C (0.5 mm): IR (liquid) 3300, 3150, 1370, 1250, 1170, and 1120 cm^{-1}; NMR ($CDCl_3$) δ 3.5 (s, 3 H), 3.7 (s, 4 H), and 6.1 (s, 1 NH); mass spectrum (CI), *m/e* 208 (M +

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H)$^+$. Anal. Calcd for $C_4H_8NO_3SF_3$: C, 23.19; H, 3.86; N, 6.76; S, 15.46; F, 27.54. Found: C, 22.94; H, 3.73; N, 6.49; S, 15.15; F, 26.95.

The trifylamide **6a** was converted to the oxamide **6** (yield, 99%) by the procedure described for 1. Vacuum distillation afforded pure **6**: bp 74–76 °C (0.5 mm); IR (liquid) 1740, 1720, 1420, 1320, 1200, 1160, and 1120 cm^{-1}; NMR ($CDCl_3$) δ 3.4 (s, 3 H), 3.7 (t, 2 H, J = 6 Hz), and 4.0 (t, 2 H, J = 6 Hz); mass spectrum (CI), m/e 461 (M + H)$^+$. Anal. Calcd for $C_{10}H_{14}N_2O_8S_2F_6$: C, 25.64; H, 2.99; N, 5.98; S, 13.68; F, 24.36. Found: C, 25.60; H, 3.11; N, 5.77; S, 13.92; F, 23.95.

***N,N'*-Bis(2-chloroethyl)-*N,N'*-bis(trifluoromethylsulfonyl)oxamide (7).** To a suspension of (2-chloroethyl)amine hydrochloride (5.80 g; 0.05 mol) and powdered 3A molecular sieves (15 g, from Linde Division, Union Carbide Corp.) in dichloroethane (100 mL) was added dropwise trifluoromethanesulfonyl chloride (5.3 mL; 0.025 mol) at room temperature under a nitrogen atmosphere. After the addition was completed, the mixture was stirred at 80 °C for 20 h. Filtration of the solid from the reaction mixture, followed by evaporation of the filtrate, gave 3.26 g (31%) of crude liquid product. Vacuum distillation of the liquid gave pure *N*-(2-chloroethyl)trifluoromethylsulfonamide (**7a**): bp 53–55 °C (0.5 mm); IR (liquid) 3310, 3150, 1420, 1370, 1220, 1200, and 1150 cm^{-1}; mass spectra (CI), m/e 212 (M + H)$^+$. Anal. Calcd for $C_3H_5NO_2SClF_3$: C, 17.06; H, 2.37; N, 6.64; S, 15.17; Cl, 16.59; F, 27.01. Found: C, 17.42; H, 2.51; N, 6.54; S, 15.38; Cl, 16.21; F, 26.79.

Oxalyl chloride (0.58 mL; 0.0067 mol) was added dropwise into a solution of **7a** (2.80 g; 0.013 mol) and "Proton Sponge" (1.44 g; 0.0067 mol, from Aldrich Chemical Co., Inc.) in methylene chloride (50 mL) at 0 °C under a nitrogen atmosphere. After the addition, the mixture was stirred at room temperature for 24 h. Solvent was evaporated, and the residue was treated with diethyl ether. The ethereal solution was dried over sodium sulfate. Evaporation of ether followed by the treatment of the residue with petroleum ether gave 2.55 g (80%) of crude product. Recrystallization of the crude product from petroleum ether afforded pure **7**: mp 71–73 °C; IR (CH_2Cl_2) 1720, 1400, 1360, 1320, 1230, 1160, and 1120 cm^{-1}; mass spectrum (CI), m/e 477 (M + H)$^+$. Anal. Calcd for $C_8H_8N_2O_6S_2Cl_2F_6$: C, 20.17; H, 1.68; N, 5.88; S, 13.45; Cl, 14.71; F, 23.95. Found: C, 20.05; H, 1.49; N, 5.92; S, 13.20; Cl, 14.98; F, 23.60.

***N,N'*-Bis(2-chloro-3-pyridyl)-*N,N'*-bis(trifluoromethylsulfonyl)oxamide (8).** To a suspension of 2-chloro-3-aminopyridine (5.14 g; 0.04 mol) and powdered 3A molecular sieves (10 g) in methylene chloride (60 mL) was added dropwise trifluoromethanesulfonic anhydride (3.4 mL; 0.02 mol) at 0 °C under a nitrogen atmosphere. After the addition was completed, the mixture was stirred at room temperature for 5 h, and then the solid was filtered. Filtrate was evaporated and treated with water to give 5.0 g (48%) of crude solid product. It was collected and recrystallized from cyclohexane to give pure *N*-(2-chloro-3-pyridyl)trifluoromethylsulfonamide (**8a**): mp 120–122 °C; IR (CH_2Cl_2) 3300, 1370, 1230, 1210, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.35 (m, 1 H), 8.0 (2 d, 1 H, J = 4 Hz), 8.35 (2 d, 1 H, J = 4 Hz), and 8.30 (s 1 NH); mass spectrum (EI), m/e 260 (M$^+$). Anal. Calcd for $C_6H_4N_2O_2SClF_3$: C, 27.69; H, 1.54; N, 10.77; S, 12.31; Cl, 13.46; F, 21.92. Found: C, 27.85; H, 1.41; N, 11.00; S, 11.95; Cl, 13.66; F, 21.50.

Oxalyl chloride (0.53 mL; 0.006 mol) was added dropwise into a stirring suspension of **8a** (2.61 g; 0.01 mol) and powdered 3A molecular sieves (5.0 g) in methylene chloride (75 mL) at 0 °C under a nitrogen atmosphere. The mixture was then heated to 60 °C, held there for 3 h, and then held at room temperature for 60 h. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The resulting residue was extracted with diethyl ether, and the combined ethereal extracts were dried over sodium sulfate. Evaporation of the dried ethereal solution obtained 2.33 g (81%) of crude product. Recrystallization of the crude product from cyclohexane gave pure **8**: mp 104–106 °C; IR (CH_2Cl_2) 1750, 1730, 1420, 1360, 1220, and 1130 cm^{-1}; NMR ($CDCl_3$) δ 7.50 (m, 1 H), 8.10 (2 d, 1 H, J = 4 Hz), and 8.5 (m, 1 H); mass spectrum (EI), m/e 574 (M$^+$). Anal. Calcd for $C_{14}H_6N_2O_6S_2Cl_2F_6$: C, 29.27; H, 1.05; N, 9.76; S, 11.15; Cl, 12.20; F, 19.86. Found: C, 29.10; H, 1.14; N, 9.90; S, 10.89; Cl, 11.95; F, 19.40.

Registry No. 1, 71537-30-9; **1a**, 23384-04-5; **2**, 71537-31-0; **2a**, 23383-96-2; **3**, 71549-42-3; **3a**, 23384-20-5; **4**, 71537-32-1; **4a**, 23383-97-3; **5**, 71549-43-4; **5a**, 23383-95-1; **6**, 71537-33-2; **6a**, 65832-23-7; **7**, 71537-34-3; **7a**, 71537-35-4; **8**, 71537-36-5; **8a**, 58157-01-0; 4-chloroaniline, 106-47-8; trifluoromethanesulfonic anhydride, 358-23-6; oxalyl chloride, 79-37-8; 2,4-dichloroaniline, 554-00-7; 2,4,5-trichloroaniline, 636-30-6; 2,4,6-trichloroaniline, 634-93-5; 4-nitroaniline, 100-01-6; 2-methoxyethylamine, 109-85-3; 2-chloroethylamine hydrochloride, 870-24-6; 2-chloro-3-aminopyridine, 6298-19-7; trifluoromethanesulfonyl chloride, 421-83-0.

Transformation of Nitrimines to Acetylenes and Allenes. 1,3 Rearrangement of *N*-Nitroenamines to *C*-Nitro Compounds

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Nitrimines, prepared from ketoximes and nitrous acid, can be converted to acetylenes and allenes by treatment with excess acetic anhydride in the presence of pyridine at reflux. With 4-(dimethylamino)pyridine as catalyst, most fragmentations proceed at room temperature. Consecutive treatment of nitrimines with strong bases and aqueous acid allows their isomerization to the less stable *N*-nitroenamines which on storage revert to the parent nitrimines. Thermolysis of *N*-nitroenamines leads to α-nitroimines by 1,3 rearrangement or to the more stable 1-(alkylamino)-2-nitro-1-alkenes. The thermal rearrangement of nitrimines follows a different course and affords mainly nitronitriles by fragmentation.

In connection with other work on the chemistry of nitrimines we came across two distinct transformations which seem to be new and proceed in yields high enough to be of some preparative value. Nitrimines with neighboring methine, and particularly methylene groups, form salts with bases. For example, acidification of the salt derived from "pernitrosocamphor" (1) gave a crystalline tautomer, "isopernitrosocamphor", which on storage slowly returned to the more stable pernitrosocamphor.[1] The stable mod-

(1) Hantzsch, A.; Dollfuss F. E. *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 226–65.

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