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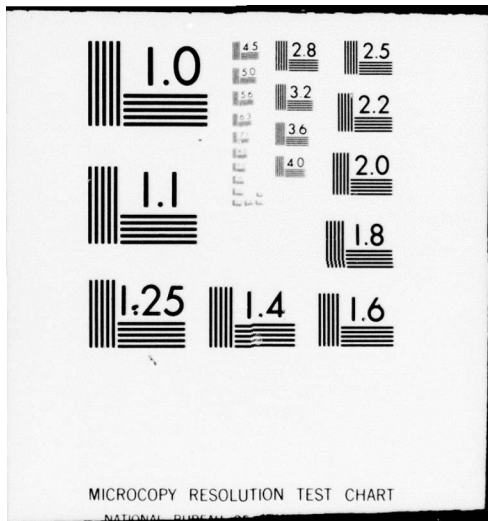
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Efficient Peroxyoxalate Chemiluminescence
from Reactions of N-Trifluoromethylsulfonyl
Oxamides with Hydrogen Peroxide and Fluorescers

by

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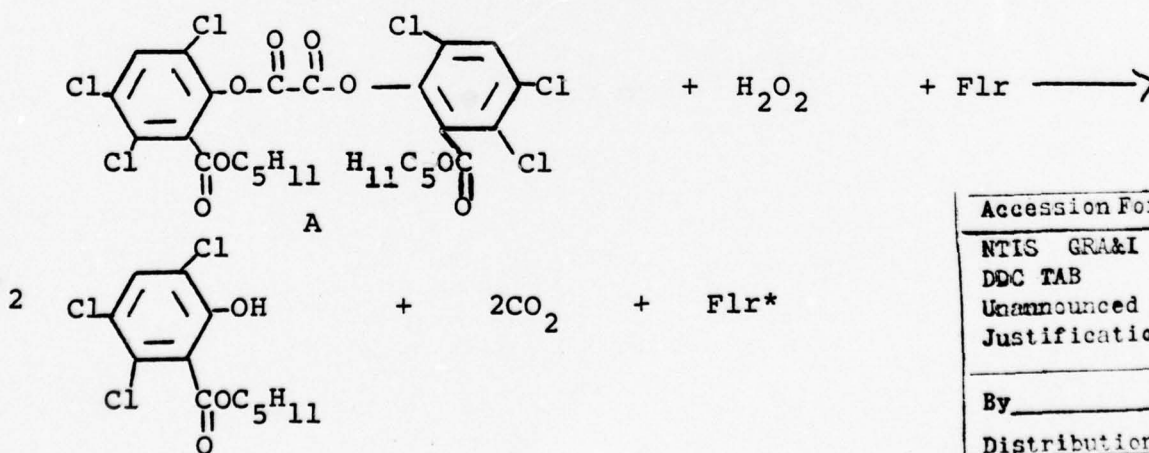
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Efficient Peroxyoxalate Chemiluminescence from Reactions of N-Trifluoromethylsulfonyl Oxamides with Hydrogen Peroxide and Fluorescers

Shin-Shyong Tseng*, Arthur G. Mohan, Linda G. Haines, Lourdes S. Vizcarra, and Michael M. Rauhut.
Contributions from the Chemical Research Division,
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Chemiluminescence quantum yields above $0.11 \text{ ein. mole}^{-1}$ (11%) 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 non-enzymatic 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 the sulfonamide.

Peroxyoxalate chemiluminescence² is illustrated by the reaction sequence outlined below:



Flr * → Flr + Light

Flr = a fluorescent compound

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Chemiluminescence quantum yields of 0.10 to 0.18 ein. mole⁻¹ (10%-18%) have been reported for the oxalic ester A with fluoresters 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) oxalate^{5,7} and bis(3-trifluoromethyl-4-nitrophenyl) oxalate⁵ have provided chemiluminescence quantum yields as high as 22 to 27%.

Other oxalic acid derivatives including mixed anhydrides⁸, amides⁸, sulfonamides⁹ and oxalyl chloride¹⁰ 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 group². In general, leaving groups containing electron attracting substituents have provided the highest efficiencies.

Results and Discussion

Inasmuch as the trifluoromethylsulfonyl (triflyl) group is one of the most powerful electron withdrawing groups known¹¹, we have investigated the chemiluminescence efficiency of a series of N-triflyl oxamides in the peroxyoxalate chemiluminescent system. The results, summarized in Table I, indicate that N-triflyloxamides which are further substituted on nitrogen by electronegatively substituted aromatic groups provide high chemiluminescence efficiency.

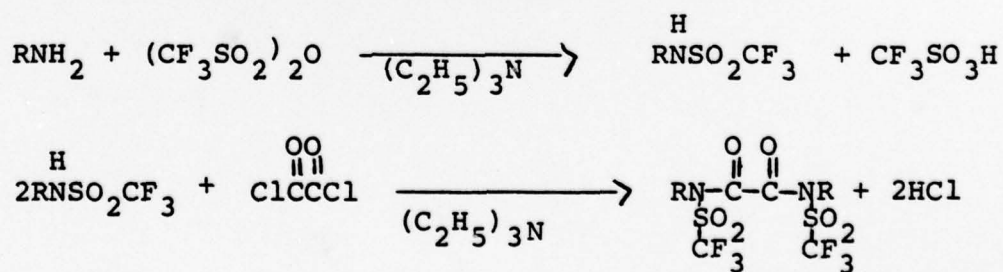
Indeed, the 2,4,5-trichloro compound 3 proved to be the most efficient non-enzymatic chemiluminescent compound yet discovered, with a chemiluminescent quantum yield of 34%.

The data in Table I indicate that increasing chlorine substitution on the aromatic ring of diphenyl triflyl oxamide 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 electro-negative than a meta¹². As expected, substitution of aliphatic groups on the nitrogens of N-triflyl oxamide resulted in substantially reduced efficiency.

The general method for preparation of the triflyl oxamides involved treatment of the amine with triflic anhydride at

Scheme I

Synthesis of N-Triflyl Oxamides



low temperature following procedures similar to those described by Hendrickson and Bergenson¹³. The acidic triflamides were then acylated with oxalyl chloride in the presence of triethyl amine to yield the desired triflyloxamides (Scheme I).

The presence of a labile chlorine atom in 2-chloroethyl trifluoromethylsulfonyl amide negated the use of triethylamine as the acid acceptor. In this case powdered 3A molecular sieves¹⁴ effectively catalyzed the sulfonamide formation, while the use of "Proton Sponge"^R, 1,8-bis(dimethylamino)-naphthalene, a strong proton acceptor but a poor nucleophile¹⁵ avoided displacement of the chlorine in reaction of the triflyamide with oxalyl chloride and afforded the oxamide in 80% crude yield. Molecular sieves were also effective catalysts for both the triflyl amide formation and the preparation of the oxamide 8. Triflylamides 4-chlorophenyl-trifluoromethylsulfonamide 1a, 2,4-dichlorophenyl-trifluoromethylsulfonamide 2a, 2,4,5-trichlorophenyl-trifluoromethylsulfonamide 3a, and 4-nitrophenyl-trifluoromethyl sulfonamide 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 electron impact (EI) mode or 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 Hirt¹⁷ modified with a Janell-Ash model 82-410 grating monochromator and an RCA C31034 photomultiplier with a gallium arsenide photocathode operated at 1300 volts with dry ice cooling. Raw data was 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 (.55) for quinine sulfate¹⁸ in .1N H₂SO₄ and by ferrioxalate actinometry¹⁹ of the exciting light.

Chemiluminescence quantum yields in einsteins mole⁻¹ of oxamides were calculated by monitoring the intensity decay at a single wavelength and calculating the intensity at each time interval in Einsteins sec⁻¹ from the chemiluminescence spectrum. Chemiluminescence spectra were corrected for intensity decay. The total area under the decay curve was calculated using a combination of a Simpson's rule integration and an exponential extrapolation to infinite time¹⁷. Data was processed via a Digital Equipment Corp. PDP-1140 computer.

4-Chlorophenyl-trifluoromethylsulfonamide (1a) To a solution of 4-chloroaniline (5.12g, 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 hours. Evaporation of the solvent gave 10.2g of light brown oil, which solidified upon standing at room temperature. Recrystallization of the solid from cyclohexane gave 9.6g (93%) of pure 1a: m.p. 45-47°C; IR (CH₂Cl₂) 3300, 1360, 1200 and 1140 cm⁻¹; NMR (CDCl₃) \int 7.2 (s, 1 NH) and 7.3 to 7.4 ppm (2 s, 4 aromatic protons); mass spectrum (EI), m/e 259 (M⁺).
Anal. Calcd for C₇H₅NO₂SClF₃: 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 (2.6g; 0.01 mol) and triethylamine (1.0g; 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 hours, heated to 60°C, held at 60°C for one hour; 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 2.46g (85%) of white crystalline 1: mp 173-174°C; IR (Nujol) 1750, 1730, 1210 and 1140 cm⁻¹; NMR (CDCl₃) ∫ 7.30 to 7.65 ppm (m, aromatic protons); mass spectrum (EI), m/e 572 (M⁺).
Anal. Calcd for C₁₆H₈N₂O₆S₂Cl₂F₆: 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 triflyl amide 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 (CDCl₃) δ 7.21 (s, 1NH) and 7.3 to 7.7 ppm (m, 3 aromatic protons); mass spectrum (EI), m/e 293 (M⁺).

Anal. Calcd for C₇H₄NO₂SCl₂F₃: 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.

Triflylamide 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 (CH₂Cl₂) 1750, 1730, 1210 and 1130 cm⁻¹; NMR (acetone - D₆) δ 7.7 and δ 7.9 ppm (aromatic protons); mass spectrum (EI), m/e 642 (M⁺).

Anal. Calcd for C₁₆H₆N₂O₆S₂Cl₄F₆: 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 triflylamide 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(CH₂Cl₂) 3300, 1360, 1210 and 1140 cm⁻¹; NMR (CDCl₃) 6.4 (s, 1NH), 7.6 and 7.8 ppm (2s, 2 aromatic protons); mass spectrum (EI), m/e 327 (M⁺).

Anal. Calcd for C₇H₃NO₂SCl₃F₃: 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 (CH₂Cl₂) 1750, 1730, 1340, 1210 and 1120 cm⁻¹; NMR (acetone-D₆), δ 7.7 and 7.9 ppm (2s, aromatic protons); mass spectrum (EI), m/e 708 (M⁺).
Anal. Calcd for C₁₆H₄N₂O₆S₂Cl₆F₆: 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) Triflylamide 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 (CH₂Cl₂) 3300, 1360 and 1160 cm⁻¹; NMR (CDCl₃) δ 6.5 (s, 1NH) and 7.8 ppm (s, 2H, 2 aromatic protons); mass spectrum (EI) m/e 327 (M⁺).
Anal. Calcd for C₇H₃NO₂SCl₃F₃: 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.

Triflylamide 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 (CDCl₃) 1740, 1380, 1260, 1210 and 1140 cm⁻¹; NMR (CDCl₃) δ 7.8 ppm (s, 4H aromatic protons); mass spectrum (EI), m/e 708 (M⁺).
Anal. Calcd for C₁₆H₄N₂O₆S₂Cl₆F₆: 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(trifluoromethyl sulfonyl) oxamide

The crude triflyl amide 5a (yield, 72%) was prepared by the procedure described for 1a: IR (CH₂Cl₂) 3250, 1350, 1220 and 1140 cm⁻¹; NMR (CDCl₃) ∫ 7.3 (s, 1NH) and 7.4 to 7.5 ppm (2s, 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(CH₂Cl₂) 1750, 1730, 1350, 1210 and 1130 cm⁻¹; NMR (CDCl₃) ∫ 7.7 to 7.9 ppm (4s, aromatic protons); mass spectrum (EI), m/e 562 (M⁺).

Anal. Calcd for C₁₆H₈N₄O₈S₂F₆: 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 triflyl amide 6a (yield, 96%) was prepared by the procedure described for 1a. Vacuum distillation afforded pure 6a: bp 50-51°C at .5 mm; IR (liquid) 3300, 3150, 1370, 1250, 1170 and 1120 cm⁻¹; NMR (CDCl₃) ∫ 3.5 (s, 3H), 3.7 (s, 4H) and 6.1 (s, 1NH); mass spectrum (CI), m/e 208 (M+H)⁺.

Anal. Calcd for C₄H₈NO₃SF₃: 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 triflyl amide 6a was converted to the oxamide 6 (yield, 99%) by the procedure described for 1. Vacuum distillation afforded pure 6: bp 74-76°C at .5mm; IR (liquid) 1740, 1720, 1420, 1320, 1200, 1160 and 1120 cm⁻¹; NMR (CDCl₃) ∫ 3.4 (s, 3H), 3.7 (t, 2H, J = 6Hz) and 4.0 ppm (t, 2H, J=6Hz); 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 (15g, from Linde Division, Union Carbide Corporation) 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 hours. Filtration of the solid from reaction mixture, followed by evaporation of the filtrate gave 3.26g (31%) of crude liquid product. Vacuum distillation of the liquid gave pure 2-chloroethyl-trifluoromethylsulfonyl amide 7a: bp 53-55°C at .5mm; IR liquid 3310, 3150, 1420, 1370, 1220, 1200 and 1150 cm^{-1} ; mass spectrum (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"^R (1.44g; 0.0067 mol, from Aldrich Chemical Company, 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 hours. 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 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 (CH₂Cl₂) 1720, 1400, 1360, 1320, 1230, 1160 and 1120 cm⁻¹; mass spectrum (CI), m/e 477 (M + H)⁺.

Anal. Calcd. for C₈H₈N₂O₆S₂Cl₂F₆: 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 (5.14g; 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 hours 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 2-chloro-3-pyridyl-trifluoromethylsulfonyl amide 8a: mp 120-122°C; IR (CH₂Cl₂) 3300, 1370, 1230, 1210 and 1140 cm⁻¹; NMR (CDCl₃) δ 7.35 (m, 1H), 8.0 (2d, 1H, J=4Hz), 8.35 (2d, 1H, J=4Hz) and 8.30 ppm (s 1NH); mass spectrum (EI), m/e 260 (M⁺).

Anal. Calcd for C₆H₄N₂O₂SClF₃: 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.

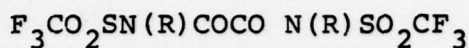
Oxalyl chloride (0.53 mL; 0.006 mol) was added dropwise into a stirring suspension of 8a (2.61 g; 0.01 mol) and powdered 3A molecular sieves (5.0g) in methylene chloride (75 mL) at 0°C under a nitrogen atmosphere. The mixture was then heated to 60°C, held thereat for 3 hours, and then at room temperature for 60 hours. 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 (CH₂Cl₂) 1750, 1730, 1420, 1360, 1220 and 1130 cm⁻¹; NMR (CDCl₃) δ 7.50 (m, 1H), 8.10 (2d, 1H, J=4HZ), and 8.5 ppm (m, 1H); mass spectrum (EI), m/e 574 (M⁺).
Anal. Calcd. for C₁₄H₆N₂O₆S₂Cl₂F₆: 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.

References and Notes

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(b) Presented in part at the 178th ACS National Meeting, Washington, D.C., September, 1979.
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TABLE I

CHEMILUMINESCENCE PERFORMANCE OF N-TRIFYL OXAMIDES^a,

COMPOUND R =	CONC M	Q.Y. ^b x 10 ⁻²	Mean Q.Y.	T.75 ^c min.	Light Capacity ^d
1 4 -chlorophenyl	.01	11.4		44.9	37.5
2 2,4-dichlorophenyl	.01	26.2		139	85.0
	.01	25.6	25.9	116	85.4
3 2,4,5-trichlorophenyl	.01	32.6		50.4	108
	.01	35.4	34.0	42.3	117
4 2,4,6-trichlorophenyl	.01	11.4		100	37.8
	.01	13.6	12.5	82.9	45.0
5 4-nitrophenyl	.01	11.0		8.88	35.7
6 2-methoxyethyl	.01	2.85		70.2	9.20
7 2-chloroethyl	.01	3.68		125	12.2
8 2-chloro-3-pyridyl	.008	15.5		129	41.3

^aChemiluminescent reactions contained the indicated concentrations of the oxamide, $6.75 \times 10^{-3} M$ 1-chloro-9,10-bis(phenylethynyl)anthracene, .375M hydrogen peroxide and $3 \times 10^{-4} M$ sodium salicylate in a solvent mixture of 75% (by volume) dibutylphthalate, 20% dimethyl phthalate, 5% t-butanol.

^bChemiluminescent quantum yield in einsteins per mole of oxamide.

^cTime required for 75% of the total light to be emitted.

^dIntegrated visible light output in lumen-hours per liter.

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