Registry No. 1 (x = I), 10364-05-3; 1 (x = Br), 89566-55-2; 1 (x = CN), 80745-57-9; 1 (x = Cl), 89566-54-1; 1 (x = $OCOCH_3$), 74467-16-6; 1 (x = F), 78385-89-4; 1 (x = CF_3), 94994-04-4; 1 (x = $C{\equiv}CSi(CH_3)_3$), 94994-11-3; 1 (x = $COCH_3$), 99631-72-8; 1 (x = $COOCH_3$), 94994-00-0; 1 (x = OCH_3), 74467-18-8; 1 (x = $Sn(CH_3)_3$), 84010-82-2; 1 (x = *p*-FC_6H_4), 61541-35-3; 1 (x = C_6H_5), 55044-15-0; 1 (x = H), 931-98-6; 1 (x = $NHCOCH_3$), 80745-58-0; 1 (x = *p*-$CH_3OC_6H_4$), 99631-73-9; 1 (x = $CON(CH_3)_2$), 80745-59-1; 1 (x = $Si(CH_3)_3$), 99631-74-0; 1 (x = CH_3), 55044-63-8; 1 (x = $N(CH_3)_2$), 80745-60-4; 1 (x = $C(CH_3)_3$), 94994-05-5; 4 (x = $Si(CH_3)_3$), 95552-61-7; 4 (x = $Sn(CH_3)_3$), 78385-88-3.

Selective Oxidation of Aldehydes to Carboxylic Acids with Sodium Chlorite-Hydrogen Peroxide

Enrico Dalcanale*

Istituto "Guido Donegani", 28100 Novara, Italy

Fernando Montanari*

Centro CNR and Dipartimento di Chimica Organica e Industriale dell'Università, 20133 Milano, Italy

Received July 23, 1985

Several methods for the oxidation of aldehydes to the corresponding carboxylic acids are known.[1,2] However, no one seems to be completely satisfactory, the major drawbacks being high costs, low selectivities, and complex operating conditions. Their application to large-scale preparations is therefore difficult.

We thus addressed our attention to the use of the inexpensive sodium chlorite,[3] which reacts with aldehydes under very mild conditions to give carboxylic acids (eq 1).

$$RCHO + HClO_2 \rightarrow RCOOH + HOCl \quad (1)$$

However, hypochlorite ion must be removed in order to avoid side reactions, since the redox pair $HOCl/Cl^-$ is a more powerful oxidant than $ClO_2^-/HOCl$.[4] Another drawback is the oxidation of ClO_2^- to ClO_2 according to eq 2.[3a,5]

$$HOCl + 2ClO_2^- \rightarrow 2ClO_2 + Cl^- + OH^- \quad (2)$$

2-Methyl-2-butene,[7a,8] resorcinol,[3a,7] and sulfamic acid[3a,9] have been tested as HOCl scavengers. 2-Methyl-2-butene must be used in a very large excess. Resorcinol is converted into 4-chloro-1,3-dihydroxybenzene, which must be removed from the reaction mixture. Sulfamic acid works well in the oxidation of hydroxylated aromatic aldehydes, but it gave poor results in the case of α,β-unsaturated aldehydes (see below).

Our HOCl scavenger was 35% H_2O_2, which reduces HOCl according to eq 3,[5] without formation of organic side products.

$$HOCl + H_2O_2 \rightarrow HCl + O_2 + H_2O \quad (3)$$

Best reaction conditions were achieved by working in a weakly acidic medium, where oxidation was rapid with no competitive reduction of $HClO_2$ to HOCl (eq 4).[5]

$$HClO_2 + H_2O_2 \rightarrow HOCl + H_2O + O_2 \quad (4)$$

$$2ClO_2 + H_2O_2 \rightarrow 2HClO_2 + O_2 \quad (5)$$

Under these conditions, any chlorine dioxide is reduced to chlorous acid (eq 5).[6,10]

Reactions were carried out by addition of 1.1-1.4 mol equiv of aqueous $NaClO_2$ to a solution of aldehyde and 1.04 mol equiv of 35% H_2O_2 in aqueous acetonitrile, at 20 °C, buffered with NaH_2PO_4 at pH 4.3. The addition of $NaClO_2$ required 1-2 h, and the reaction was complete after another 1-5 h depending on the aldehyde (procedure A). With the most sensitive substrates more H_2O_2 (up to 5 mol equiv) and a lower pH (~2) were required, in order to speed up HOCl reduction by H_2O_2. In a few instances carboxylic acids quantitatively precipitated and were directly filtered from the reaction medium. In most cases isolated yields were very high for satisfactorily pure products (Table I).

Following this procedure β-aryl-substituted α,β-unsaturated aldehydes are oxidized to the corresponding carboxylic acids without affecting the olefinic double bond (entries 1-5). Yields are lower with aliphatic α,β-unsaturated and/or more hydrophilic aldehydes (entries 19, 20). In the presence of an electron donor group in β-position (entry 21), chlorination of the double bond becomes predominant. The same occurs in the presence of isolated double bonds (entry 22). Triple bonds directly linked to the aldehyde group are substantially stable under these conditions. For example, phenylpropargylic aldehyde is converted into the corresponding carboxylic acid, together with only small amounts of benzoic acid (entry 6).

The method reported here is of general application to aromatic aldehydes, including those which are incompatible[2b] with HOCl (entries 7-9). Heterocyclic aldehydes are good substrates (entries 14-16), except for those which are sensitive to the acidic medium like pyrroles (entry 18). Furfural gives mainly 2-furoic acid with small quantities of maleic acid as a side product (entry 17).[11] *p*-Aminobenzaldehyde affords only tars (entry 12). In *p*-methylthiobenzaldehyde, oxidation of the aldehyde group is accompanied by the concomitant oxidation of sulfide to a mixture of sulfoxide and sulfone (entry 13).

The effect of various organic solvents was checked with cinnamaldehyde as substrate. Results are summarized in Table II.

The yield was increased using less hydrophilic alcohols (entries 1-4). Toluene (entry 5) greatly reduced the reaction rate, requiring 24 h for complete conversion of the substrate.

For aldehydes in which reaction of HOCl with the substrate is faster than reaction with H_2O_2 (Table I, entries 10, 11), dimethyl sulfoxide (Me_2SO) proved to be an effective HOCl scavenger when used as solvent, since it is

(1) (a) Augustine, R. L. "Oxidation"; Dekker, Inc.: New York, 1969; Vol. I, pp 81-86. (b) Buehler, C. A.; Pearson, D. E. "Survey of Organic Synthesis"; Wiley: New York, 1970; Vol. I, pp 760-764; 1977, Vol. II, p 669. (c) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw Hill: New York, 1977; p 641-643. (d) Houben-Weyl "Methoden der Organischen Chemie", Bd E 3, "Aldehyde"; Farbe, J. Ed; Georg Thieme Verlag: Stuttgart, 1983; pp 634-635. (e) Dehmlow, E. V.; Dehmlow, S. S. "Phase-Transfer Catalysis", 2nd ed.; Verlag Chemie: Weinheim, 1983; pp 295-321.

(2) (a) Ganem, B.; Heggs, R. P., Biloski, A. J.; Schwartz, D. R. *Tetrahedron Lett.* **1980**, *21*, 685-688. (b) Nwaukwa, S. O.; Keehn, P. M. *Ibid.* **1982**, *23*, 3131-3134. (c) Scholz, D. *Monatsh. Chem.* **1979**, *110*, 1471-1473.

(3) (a) Lindgren, B. O.; Nilsson, T. *Acta Chem. Scand.* **1973**, *27*, 888-890. (b) Kudesia, V. P. *Bull. Soc. Chim. Belg.* **1972**, *81*, 623-628.

(4) Holst, G. *Chem. Rev.* **1954**, *54*, 169-194.

(5) Reaction 4 is very slow in the pH range 3.5-9.0 and at low temperatures.[6]

(6) Kirk-Othmer "Encyclopedia of Chemical Technology", 3rd ed.; Wiley: New York, 1979; Vol. V, pp 585-632.

(7) (a) Bal, B. S.; Childers, W. E.; Pinnik, H. W. *Tetrahedron* **1981**, *37*, 2091-2096. (b) Kraus, G. A.; Tashner, M. J. *J. Org. Chem.* **1980**, *45*, 1175-1176. (c) Kraus, G. A.; Roth, B. *Ibid.* 4825-4830.

(8) Arora, G. S.; Shirahama, H.; Matsumato, T. *Chem. Ind.* **1983**, 318.

(9) Colombo, L.; Gennari, C.; Santandrea, M.; Narisano, E.; Scolastico, C. *J. Chem. Soc., Perkin Trans. 1* **1980**, 136-140.

(10) MacMahon, J. D. U.S. Patent 2358866, 1944; *Chem. Abstr.* **1945**, *39*, 1740.

(11) Furfural doesn't react with H_2O_2 alone under these conditions. However 2,5-di-*tert*-butylfuran is oxidized by NaOCl to 2,2,7,7-tetramethyl-4-octene-3,6-dione.[12]

(12) Fitzpatrich, J. E.; Milner, D. J.; White, P. *Synth. Commun.* **1982**, *12*, 489-494.

0022-3263/86/1951-0567$01.50/0

Table I. Oxidation of Aldehydes to Carboxylic Acids with $NaClO_2$–H_2O_2[a]

entry	substrate[b]	procedure	carboxylic acid: isolated yields, %	carboxylic acid: mp, °C[c]
1	$C_6H_5CH{=}CHCHO$	A	95[d]	131–133 (133)
2	$C_6H_5CH{=}C(CH_3)CHO$	A	93[e]	76–80 (79–81)
3	$C_6H_5CH{=}C(Cl)CHO$	A	93[f]	135–136 (137–138)
4	$C_6H_5CH{=}C(Br)CHO$	A	94[g]	129–130 (131–132)
5	o-$O_2NC_6H_4CH{=}CHCHO$	A	98	240–241 (240)
6	$C_6H_5C{\equiv}CCHO$	B	74[h]	135–136 (137)
7	C_6H_5CHO	A[i]	93	120–121 (122)
8	p-$CH_3OC_6H_4CHO$	A	86	183–184 (184)
9	p-$CH_3CONHC_6H_4CHO$	A[l]	98	258–259 (259–262)
10	p-HOC_6H_4CHO	B	7[m]	212–213 (213–214)
11	2-OH-3-$(OCH_3)C_6H_3CHO$	A, B	*n*	
12	p-$H_2NC_6H_4CHO$	A, B	*o*	
13	p-$CH_3SC_6H_4CHO$	A[p]	100[q]	
14	pyridine-4-carboxaldehyde	A	100[r]	313–315 (315)
15	thiophene-2-carboxaldehyde	A	94	127–129 (129–130)
16	5-nitrofuran-2-carboxaldehyde	B	84	183 (184)
17	furan-2-carboxaldehyde	B	82[s]	131–133 (133–134)
18	pyrrole-2-carboxaldehyde	A,B	*o*	
19	$CH_3CH_2CH_2CH{=}CHCHO$	A	88	36–37 (36–37)
20	$CH_3CH{=}CHCHO$	B	53[t]	71–72 (72)
21	$C_2H_5OCH{=}C(CH_3)CHO$	A,B	*n*	
22	$(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCHO$ (cis and trans)	A,B	*n*	
23	$CH_3CH_2CH_2CH_2CH_2CHO$	A	96	127–129 (760 torr)
24	2-$CH_3C_6H_4CHO$	A	91	101–103 (102–103)

[a] Acetonitrile as solvent, unless otherwise stated. [b] α,β-Unsaturated aldehydes and acids are *E* diastereoisomers, unless otherwise stated. [c] Crude products. In parenthesis, mp or bp values from the literature.[13] [d] A small amount (<2%) of β-chlorostyrene was also formed. Mass spectrum, *m/e* 138 (M^+), 103 (100%), 77, 51. [e] ^1H NMR ($CDCl_3$) δ 2.11 (d, 3 H), 7.32 (d, 5 H), 7.75 (d, 1 H), 11.70 (s, 1 H). [f] ^1H NMR ($CDCl_3$) δ 7.30–7.61 (m; 3 H), 7.70–7.96 (m, 2 H), 8.00 (s, 1 H), 12.50 (s, 1 H). [g] ^1H NMR ($CDCl_3$) δ 7.25–7.55 (m, 3 H), 7.65–8.05 (m, 2 H), 8.31 (s, 1 H), 12.30 (s, 1 H). [h] Benzoic acid (6%) was also formed. [i] CH_3OH as solvent. [l] CH_3OH–CH_3CN 1:1 as solvents. [m] Hydroquinone (27%), mp 170 °C, was the main product, together with chlorinated compounds and tars. [n] Chlorinated compounds, only. [o] Tars. [p] Molar ratio $NaClO_2$-aldehyde 1:1. [q] Gas chromatographic yields: mixture of p-$CH_3SOC_6H_4COOH$ (75%), and p-$CH_3SO_2C_6H_4COOH$ (25%) (^1H NMR analysis). Mass spectra (methyl esters): sulfoxide, *m/e* 198 (M^+), 183, 151 (100%), 77, 59, 45; sulfone, *m/e* 214 (M^+), 198, 183, 151 (100%), 77, 59, 45. [r] Mass spectrum (methyl ester): *m/e* 137 (M^+), 106, 78 (100%), 59. [s] Maleic acid (15%), mp 129–130 °C, was also formed. [t] No other products except tars were detected.

Table II. Oxidation of Cinnamaldehyde with $NaClO_2$–H_2O_2 in Various Solvents

entry	solvent	isolated yields, %
1	MeOH	89
2	EtOH	91
3	*i*-BuOH	95
4	*t*-BuOH	95
5	Toluene	95
6		95

Table III. Oxidation of Aldehydes to Carboxylic Acids with $NaClO_2$–Me_2SO

entry	substrate	carboxylic acid: isolated yields, %	carboxylic acid: mp,[a] °C
1	$C_6H_5CH{=}CHCHO$	95	130–132 (133)
2	p-HOC_6H_4CHO	86	211–214 (213–214)
3	2-HO-3-$(CH_3O)C_6H_3CHO$	83	148–149 (152)
4	$(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCHO$ (cis and trans)	46[c]	
5	cyclohex-3-ene carboxaldehyde	30[d]	

[a] Crude products. In parentheses, melting point values from the literature.[13] [b] *E/Z* = 58:42. [c] Gas chromatographic yields at 67% conversion: *E/Z* = 71:29. With an aldehyde/$NaClO_2$ 1:3 molar ratio, only a 30% yield of carboxylic acids (*E/Z* = 70:30) was observed at 100% conversion, the remaining being chlorinated compounds. [d] Gas chromatographic yields, the remaining being chlorinated and hydroxylated compounds.

oxidized to dimethyl sulfone. Results are summarized in Table III.

Me_2SO works well with α,β-unsaturated aldehydes, such as cinnamaldehyde (entry 1), and with aromatic hydroxy aldehydes (entries 2, 3). Fair results were obtained in the presence of isolated C=C double bonds (entries 4,5). In all cases, reaction rates were lower and the workup more difficult than for reactions carried out in the presence of H_2O_2. It must be noted that, in the oxidation of cinnamaldehyde, sulfamic acid was also tested as HOCl scavenger: cinnamic acid was isolated in fair yields (60%), together with minor amounts of cinnamonitrile.

In conclusion, the use of the inexpensive pair $NaClO_2$–H_2O_2 or, in some cases, of $NaClO_2$–Me_2SO, allows mild oxidation of a wide range of aromatic, aliphatic, and heterocyclic aldehydes to the corresponding carboxylic acids. This method is particularly useful for substrates in which other oxidation methods fail or require complex and expensive reaction conditions.

Experimental Section

^1H NMR Spectra were recorded at 60 and 90 MHz on Hitachi Perkin-Elmer R-24 B and Brücker W-90 spectrometers, respectively, with Me_4Si as internal standard. Mass spectra were obtained with a CHS-DF Varian MAT-GC/MS spectrometer and IR spectra with Pye-Unicam SP3-100 spectrophotometer. GLC analyses were performed on Hewlett-Packard Models 7620 A and 5830 A flame-ionization instruments with Supelco SP-2100 columns. Melting points were measured on a Büchi-Tottoli apparatus and are uncorrected.

Organic and inorganic reagents, ACS grade, were used without further purification. All products were identified through their mp, ^1H NMR spectra, and/or IR and MS spectra.

General Oxidation Procedures. Procedure A. A solution of 8.0 g (7.0×10^{-2} mol) of $NaClO_2$ (79% purity, by iodometric titration) in 70 mL of water was added dropwise in 2 h to a stirred mixture of 6.6 g (5×10^{-2} mol) of cinnamaldehyde (99% purity) in 50 mL of acetonitrile

and 1.6 g of NaH_2PO_4 in 20 mL of water and 5.0 mL (5.2 × 10^{-2} mol) of 35% H_2O_2, keeping the temperature at 10 °C with water cooling. Oxygen evolved from the solution was monitored until the end of the reaction (about 1 h) with a bubbler connected to the apparatus. A small amount (~0.5 g) of Na_2SO_3 was added to destroy the unreacted HOCl and H_2O_2. Acidification with 10% aqueous HCl afforded 7.0 g (95%) of cinnamic acid, as crystalline solid, mp 131–133 °C (lit.[13] mp 133 °C). TLC and GLC analyses revealed not valuable impurities. ^1H NMR ($CDCl_3$) δ 6.41 (d, 1 H), 7.17–7.69 (m, 5 H), 7.73 (d, 1 H), 11.85 (s, 1 H).

Procedure B. It differs from procedure A since a 5:1 molar ratio H_2O_2–aldehyde is used, and the pH of the medium is lowered to about 2.0 by cautious addition of 37% HCl to the NaH_2PO_4 buffer. The reactions are faster than those of procedure A.

General Oxidation Procedure with $NaClO_2$–Me_2SO. A solution of 8.0 g (7.0 × 10^{-2} mol) of 79% $NaClO_2$ (iodometric titration) in 70 mL of H_2O was added dropwise in 2 h at room temperature to a stirred mixture of 6.6 g (5.0 × 10^{-2} mol) of cinnamaldehyde in 50 mL of Me_2SO and of 1.6 g of NaH_2PO_4 in 20 mL of water. The mixture was left overnight at room temperature, then 5% aqueous solution of $NaHCO_3$ was added. The aqueous phase was extracted 3 times with CH_2Cl_2 and acidified with 10 M aqueous HCl, and the precipitated cinnamic acid was collected: 7.0 g (95% yield), mp 130–132 °C. TLC and GLC analyses revealed no appreciable impurity nor contamination from Me_2SO or dimethyl sulphone.

General Oxidation Procedure with $NaClO_2$–H_2NSO_3H. The general procedure A was followed, but 6.3 g (6.5 × 10^{-2} mol) of sulfamic acid as scavenger dissolved in 60 mL of water and 6.6 g (5 × 10^{-2} mol) of cinnamaldehyde in 50 mL of *tert*-butyl alcohol was used. After 2 h at room temperature, a crude product was isolated and purified by column chromatography (silica gel; 8:2 ethyl ether–*n*-hexane): 4.4 g (60%) of cinnamic acid, mp 131–133 °C, 1.64 g (25%) of cinnamonitrile, mp 20 °C (lit.[13] mp 20–21 °C), and 0.1 g (1.2%) of *tert*-butyl cinnamate, bp 70 °C (0.1 torr) (lit.[13] bp 140 °C (9 torr)).

Acknowledgment. We are grateful to Dr. R. Santi for helpful discussions and to Mrs. T. Fiorani for determination of the mass spectra.

Registry No. (*E*)-C_6H_5CH=CHCHO, 14371-10-9; (*E*)-C_6H_5CH=C(CH_3)CHO, 15174-47-7; (*E*)-C_6H_5CH=C(Cl)CHO, 99414-74-1; (*E*)-C_6H_5CH=C(Br)CHO, 99686-39-2; (*E*)-*o*-$O_2NC_6H_4CH$=CHCHO, 66894-06-2; p-$CH_3CONHC_6H_4CHO$, 122-85-0; p-HOC_6H_4CHO, 123-08-0; (*E*)-CH_3CH=CHCHO, 123-73-9; (*E*)-C_2H_5OCH=C(CH_3)CHO, 62055-46-3; (*Z*)-$(CH_3)_2C$=$CH(CH_2)_2C(CH_3)$=CHCHO, 106-26-3; (*E*)-$(CH_3)_2C$=$CH(CH_2)_2C(CH_3)$=CHCHO, 141-27-5; $CH_3(CH_2)_4CHO$, 66-25-1; (*E*)-C_6H_5CH=$CHCO_2H$, 140-10-3; (*E*)-C_6H_5CH=$C(CH_3)CO_2H$, 1895-97-2; (*E*)-C_6H_5CH=C(Cl)CO_2H, 705-55-5; (*E*)-C_6H_5CH=C(Br)CO_2H, 15894-30-1; (*E*)-*o*-$O_2NC_6H_4CH$=$CHCO_2H$, 882-06-4; $C_6H_5C{\equiv}CCO_2H$, 637-44-5; p-$CH_3CONHC_6H_4CO_2H$, 556-08-1; p-$CH_3SOC_6H_4CO_2H$, 33963-58-5; p-$CH_3SO_2C_6H_4CO_2H$, 4052-30-6; (*E*)-$CH_3(CH_2)_2CH$=$CHCO_2H$, 13419-69-7; (*E*)-CH_3CH=$CHCO_2H$, 107-93-7; 2-HO-3-$CH_3OC_6H_3CO_2H$, 877-22-5; (*E*)-$(CH_3)_2C$=$CH(CH_2)_2C(CH_3)$=$CHCO_2H$, 4698-08-2; (*Z*)-$(CH_3)_2C$=$CH(CH_2)_2C(CH_3)$=$CHCO_2H$, 4613-38-1; C_6H_5C<<-tbdCCHO, 2579-22-8; C_6H_5CHO, 100-52-7; p-$CH_3OC_6H_4CHO$, 123-11-5; 2-OH-3-$(OCH_3)C_6H_3CHO$, 148-53-8; p-$H_2NC_6H_4CHO$, 556-18-3; p-$CH_3SC_6H_4CHO$, 3446-89-7; 2-$CH_3C_6H_4CHO$, 529-20-4; $C_6H_5CO_2H$, 65-85-0; p-$CH_3COC_6H_4CO_2H$, 100-09-4; $CH_3(CH_2)_4CO_2H$, 142-62-1; 2-$CH_3C_6H_4CO_2H$, 118-90-1; $NaClO_2$, 7758-19-2; H_2O_2, 7722-84-1; Me_2SO, 67-68-5; H_2NSO_3H, 5329-14-6; pyridine-4-carboxaldehyde, 872-85-5; thiophene-2-carboxaldehyde, 98-03-3; 5-nitro-2-furancarboxaldehyde, 698-63-5; furan-2-carboxaldehyde, 98-01-1; pyrole-2-carboxaldehyde, 1003-29-8; hydroquinone, 123-31-9; methyl pyridine-4-carboxylate, 2459-09-8; 5-nitro-2-furancarboxylic acid, 645-12-5; 2-furancarboxylic acid, 88-14-2; maleic acid, 110-16-7; cyclohexene-3-carboxaldehyde, 100-50-5; cyclohexene-3-carboxylic acid, 4771-80-6; thiophene-2-carboxylic acid, 527-72-0.

(13) Buckingham, J. "Dictionary of Organic Compounds", 5th ed.; Chapman and Hall: New York, 1982.

Synthesis of Novel 6*H*-1,3-Oxazine Derivatives with Perfluoroalkyl Substituents

Isao Ikeda,* Mitsuhiro Umino, and Mitsuo Okahara

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka, Japan 565

Received October 2, 1985

Recently, the reactions of perfluoro-2-methylpent-2-ene (**1**),[1,2] a dimer of hexafluoropropene, with various nucleophiles such as alcohols, carboxylic acids, amines and thiols (or their conjugate bases) have been investigated,[3,4] and it has been reported that the reaction proceeded via an apparent nucleophilic substitution reaction.

The reaction of **1** as a 1,3-bidentate electrophile has been studied in recent years and various heterocycles with five-, six-, seven-, and eight-membered rings resulted from the reactions with bidentate nucleophiles such as *N,N*-dimethylhydrazine,[5] acylhydrazones,[6] benzoylacetonitrile, benzoyltrifluoroacetone, acetoacetanilide, catechol, *o*-phenylenediamine, *o*-aminophenol, and salicylaldehyde.[7-9]

In the present work, new 6*H*-1,3-oxazines with perfluoroalkyl substituents (**3a–d**) were obtained in moderate yields from **2** and **1** in the presence of base.

Results and Discussion

When a tetrahydrofuran (THF) solution of **1** was treated with a THF suspension of the sodium salt of **2a**, a single oxazine was cleanly formed as demonstrated by ^{19}F NMR. The spectrum of the product showed the presence of only one pentafluoroethyl, one trifluoromethyl, and one difluoromethylene group. However, spectral data did not rule out one of the two possible structures (**3a** and **4a**). To distinguish between these two possibilities, the product was treated with 1,1-dimethylhydrazine.[10] The ^{19}F NMR spectrum of the resulting compound showed the disappearance of two fluorine atoms from the original product (**3a** or **4a**); a band assigned to carbonyl absorption (1720 cm^{-1}) appeared in the IR spectrum. Furthermore, the mass spectrum of the dimethylhydrazine-treated product displayed a very strong fragment of relative abundance of 69

(1) Du Pont U.S. Patent 2918501, 1959.
(2) Dresdner, R. D.; Tlumac, F. N.; Young, J. A. *J. Org. Chem.* **1965**, *30*, 3524.
(3) Ishikawa, N.; Nagashima, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 502.
(4) Yanagida, S.; Noji, Y.; Okahara, M. *Tetrahedron Lett.* **1977**, 2337.
(5) Ikeda, I.; Tsukamoto, T.; Okahara, M. *Chem. Lett.* **1980**, 583.
(6) Ikeda, I.; Kogame, Y.; Okahara, M. *J. Org. Chem.* **1985**, *50*, 3640.
(7) Flowers, W. T.; Haszeldine, R. N.; Owen, C. R.; Thomas, A. *J. Chem. Soc., Chem. Commun.* **1974**, 134.
(8) Maruta, M.; Kubota, S.; Yoshimura, N.; Kitazume, T.; Ishikawa, N. *J. Fluorine Chem.* **1980**, *16*, 75.
(9) Maruta, M.; Kubota, S.; Yoshimura, N.; Kitazume, T.; Ishikawa, N. *Chem. Lett.* **1979**, 291.
(10) Zentmyer, D. T.; Wagner, E. C. *J. Org. Chem.* **1949**, *14*, 967.

0022-3263/86/1951-0569$01.50/0