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DIFLUOROMETHANESULFONIC ACID. I. AN IMPROVED ROUTE TO SODIUM DIFLUOROMETHANESULFONATE

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SUMMARY

The synthesis of sodium difluoromethanesulfonate from aqueous sodium sulfite and chlorodifluoromethane became productive, more selective and reproducible by adding sodium hydroxide, even in quantities smaller than the stoichiometry. This reaction has been optimized and its carbenic nature unambiguously proved by conducting the reaction in deuterium oxide. "Sodium diflate" could also be formed from sodium sulfite and dibromodifluoromethane by another carbenic process.

INTRODUCTION

Recent progress in the synthesis of perfluorinated sulfonic acids, mainly trifluoromethanesulfonic acid ('triflic acid') [1,2], prompted us to report some results we patented several years ago [3,4] concerning the manufacture of difluoromethanesulfonic acid, which could be named 'diflic acid by analogy with its trifluoro analog. Diflic acid is less acidic than triflic acid but cheaper, as will be seen, and

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its acidity is often sufficient to catalyse, as does triflic acid, electrophilic reactions [5-12] since the cologarithm of its dissociation constant in glacial acetic acid is 5.7, compared to 4.7 for triflic acid and 7.0 for sulfuric acid [7]. Moreover, an acid weaker than CF_3SO_3H can be of some interest for reaction selectivities, as illustrated by the acid-catalyzed hydration of propene [5]:

$$CH_3{-}CH{=}CH_2 + H_2O \xrightarrow[200°C/1.5\ h]{4.10^{-3}\ mole\ XCF_2SO_3H} (CH_3)_2CH{-}OH$$

X= F	conv.= 66.5%	selectivity= 37.7%
X= H	conv.= 53.3%	selectivity= 98%

On the other hand, several derivatives of diflic acid, like difluoromethyl diflate are valuable neutral precursors of difluorocarbene, either in basic or acidic media [13-15].

Taking note of its advantages, we decided to explore the synthesis of this poorly known acid.

Difluoromethanesulfonyl fluoride has been synthesized for the first time through decarboxylative hydrolysis of carboxydifluoromethanesulfonyl fluoride [16-18]. Later, difluoromethanesulfonyl chloride was obtained by chlorination of benzyl difluoromethyl thioether in water [19-21]. Diflic acid itself has been detected among the products of oxyfluorination of dichloromethanethiol [22] and, more recently, has been produced through the acidification of potassium diflate [7]. This salt was obtained from potassium sulfite and chlorodifluoromethane by analogy with an old publication of Farrar describing the formation of sodium diflate in a rather modest yield [23]:

$$CHF_2Cl + Na_2SO_3 \xrightarrow[120°C/16\ bar/20\ h]{H_2O} CHF_2SO_3Na + NaCl$$

Yield= 23%

This route was long considered unworkable because it "has proven complicated and inefficient (10–20% yields) for larger runs [and] unreliable.[...]Yields in this step were particularly erratic for CHF_2Cl (several <10%)" [19]. However, as this pathway remained, without any doubt, the most economic route to diflic acid, we tried to improve it.

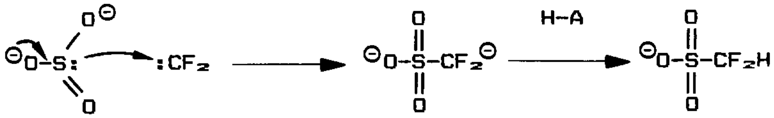
RESULTS AND DISCUSSION

Sodium difluoromethanesulfonate from chlorodifluoromethane. Parametric study

It is now well established that chlorodifluoromethane cannot be involved in SN2 mechanisms [24] but delivers difluorocarbene readily in basic media [25]. Thus, the reaction of sodium sulfite upon chlorodifluoromethane could be understood as a carbenic process, sodium sulfite being the base (O-attack) and the nucleophile (S-attack). The poor basicity of sulfite anion could thus explain the low yield of sodium diflate. Other indications of such a mechanism can be drawn from the comparison of the reactions of sodium sulfite with several haloforms [23]: the reactivity follows the acidities of the haloforms and the stabilities of the halocarbenes ($CHF_2Cl > CHFCl_2 > CHCl_3 > CH_2FCl$ and $:CF_2 > :CFCl > :CCl_2 > :CHF$) [25d].

Thus, we postulated the following scheme I:

$$SO_3^{2\ominus} + CHF_2Cl \longrightarrow HSO_3^{\ominus} + :CF_2 + Cl^{\ominus}$$



Scheme I

This hypothesis was supported by our preliminary experiments:

1°- reaction between chlorodifluoromethane and two different commercial sodium sulfites, under Farrar's conditions, delivered a sodium diflate yield of 24% (sulfite A) and 0.5% (sulfite B). Though the sulfite purities were proved to be of the same order by chemical analysis, the pH (at 25°C) of their centimolar aqueous solutions were found significantly different (9.26 (sulfite A) and 9.16 (sulfite B)). This difference corresponded to an excess of 0.05 mole NaOH/mole Na_2SO_3 for sulfite A v.s. sulfite B.

2°- when adding 1 mole of sodium hydroxide per mole of sodium sulfite B and reacting this mixture with chlorodifluoromethane, under Farrar's conditions, a 11% sodium diflate yield was obtained (compared to 0.5% yield in the previous experiment). In addition, fluoride anions were also found and could result from the known basic hydrolysis of difluorocarbene when the hydroxyl anion acts as a nucleophile:

$$:CF_2 + 2\ HO^{\ominus} \longrightarrow CO + 2\ F^{\ominus} + H_2O$$

(CO could be qualitatively observed in all experiments with specific security detectors).

The influence of temperature, molar ratios and concentrations was examined, using sulfite B as reagent. The results are summarized in Table I. Four criteria were checked to compare the results of the experiments:

R1= (produced ion-g $Cl^{\ominus}$/introduced moles CHF_2Cl) x 100

R2= (ion-g $CHF_2SO_3^{\ominus}$/ion-g $Cl^{\ominus}$) x 100

R3= (0.5 (ion-g $F^{\ominus}$/ion-g $Cl^{\ominus}$)) x 100

R4= (moles CHF_2SO_3Na/introduced moles Na_2SO_3) x 100

R1 measured the chlorodifluoromethane conversion, R2 the selectivity of formation of sodium diflate v.s. consumed CHF_2Cl, R3 the selectivity of hydrolysis of chlorodifluoromethane and R4 the yield of production of sodium diflate v.s. introduced sulfite. In every case, it has been noted that R2+R3 < 100, indicating that some volatile products (eventually fluoroolefins resulting from polymerization of difluorocarbene) escaped the analysis.

Influence of the temperature

It can be seen from entries 1 and 2 in Table I that the selectivities of diflate formation and CHF_2Cl hydrolysis remained roughly constant while the CHF_2Cl conversion increased between 120°C and 150°C. This would be consistent with the proposed carbenic process: CHF_2Cl deprotonation increased and the ratio between sulfite and hydroxyl nucleophilicities remained constant. The contrary was true between 150°C and 180°C (entries 2 and 3): CHF_2Cl conversion remained constant but diflate selectivity doubled, perhaps because of a lesser hydration of the sulfite anion. However, if yields were higher at 180°C, corrosion of the stainless steel vessel became too extensive and 150°C was chosen as the optimum temperature.

Influence of the ratio sodium hydroxide/sodium sulfite

Comparison of entries 2, 4 and 5 or 6 and 7 or 8 and 9 showed that increasing amounts of sodium hydroxide enhanced the conversion of CHF_2Cl but also the hydrolysis of difluorocarbene while the diflate formation selectivity reached a maximum for values of $NaOH/Na_2SO_3$ between 0.1 to 0.5 . Globally, sodium diflate yield (v.s. sulfite) also reached a maximum value for $NaOH/Na_2SO_3$ ratios between 0.1 and 0.5 . The dramatic effect of small amounts of sodium hydroxide are in accord with the carbenic mechanism postulated in Scheme II:

TABLE I

Entry	F22* / Na_2SO_3	H_2O** / Na_2SO_3	NaOH / Na_2SO_3	Temp. (°C)	P (bar)	R1	R2	R3	R4	R2 +R3
1	2	333	1	120	16	19.5	28	39	11	67
2	3	333	1	150	60	34.7	29	41	29	70
3	3	333	1	180	100	32.7	56	35	55	91
2	3	333	1	150	60	34.7	29	41	29	70
4	3	333	0.5	150	60	32.3	38	31	36.5	69
5	3	333	0.1	150	60	21.3	43	10	27.5	53
6	1.5	417	0.5	150	43	62.3	54.5	39	51	93.5
7	1.5	417	0	150	43	46.6	24		17	
8	1	626	0.55	120	16	81	56		45	
9	1	626	0.05	120	16	59	40.5		24	
2	3	333	1	150	60	34.7	29	41	29	70
10	3	167	1	150	70	23	26	73	18	99
6	1.5	417	0.5	150	43	62.3	54.5	39	51	93.5
4	3	333	0.5	150	60	32.3	38	31	36.5	69
11	3	167	0.5	150	70	33.3	19	30	19	49
5	3	333	0.1	150	60	21.3	43	10	27.5	53
12	3	167	0.1	150	70	17.7	29	32	15	61
5	3	333	0.1	150	60	21.3	43	10	27.5	53
13	1	333	0.1	150	43	64	42	20	27	62

* F22= chlorodifluoromethane ** ml/mole Na_2SO_3= sulfite B

$$HO^{\ominus} + H\text{-}CF_2\text{-}Cl \longrightarrow H_2O + {:}CF_2 + Cl^{\ominus}$$

$$SO_3^{\ominus} + {:}CF_2 \longrightarrow {}^{\ominus}O\text{-}SO_2\text{-}CF_2^{\ominus}$$

$${}^{\ominus}O\text{-}SO_2\text{-}CF_2^{\ominus} + H_2O \longrightarrow {}^{\ominus}O\text{-}SO_2\text{-}CF_2H + HO^{\ominus}$$

Scheme II

The decrease of sodium diflate selectivity when the amount of sodium hydroxide reached the stoichiometry could result from a partial salting-out of poorly soluble sodium sulfite by very soluble sodium hydroxide.

Influence of the dilution

Entries 2, 10 or 6, 4, 11 or 5, 12 have to be compared. Though results were a little difficult to explain entirely because dilution should interfere at both concentrations, there was no doubt that the concentration of sodium sulfite, the less soluble reagent, was the most affected. Indeed, sodium diflate selectivity was improved by dilution. In order to keep a reasonable productivity, 400 to 450 ml water/mole sodium sulfite were found optimum.

Influence of excess chlorodifluoromethane

Comparison of entries 5 and 13 showed that an excess of CHF_2Cl had no effect. The rate of dissolution of CHF_2Cl is probably the limiting factor.

Influence of the cation

When replacing the system $Na_2SO_3/NaOH$ by K_2SO_3/KOH, the following results were obtained:

$$\underset{3eq.}{CHF_2Cl} + \underset{1\ eq.}{M_2SO_3} \xrightarrow[150°C/60\ bar/20\ h]{MOH\ (1\ eq.)/H_2O\ (333\ ml)} CHF_2SO_3M + MCl$$

TABLE II

Entry	M	R1	R2	R3	R2 + R3	R4
2	Na	34.7	29	41	70	29
15	K	50	27	15	42	40.5

Potassium sulfite is known to be three times more soluble than sodium sulfite [26] and more dissociated. That could explain the higher ratio R2/R3 observed when K_2SO_3 was used, $SO_3^{=}$ being a better nucleophile than OH^- provided that it was sufficiently available(Table II). On the other hand, KOH is also known to be more basic than NaOH, explaining the higher conversion of CHF_2Cl, which could also result from an enhanced basicity of the sulfite anion in K_2SO_3.However,the use of potassium cations enhanced the basicities of both sulfite and hydroxyl anions more than their nucleophilicities as volatile products were more abundant when employing K_2SO_3 and KOH.

Mechanistic investigations

D_2O as solvent

All these results were compatible with the carbenic chain process postulated in Scheme II but it was of some interest to corroborate it by a non ambiguous proof. For that purpose, an experiment was performed under the conditions indicated in entry 6 (Table I) but using deuterium oxide as solvent instead of water: the isolated difluorosulfonate produced was proved to be, by ^1H, ^{19}F and ^2D NMR analysis, a mixture of 99.5% CDF_2SO_3Na and 0.5% CHF_2SO_3Na. As Moore has already demonstrated that chlorodifluoromethane did not exchange with DOH/D_2O [19] and as we verified that no isotopic exchange occurred in CDF_2SO_3Na/H_2O and CHF_2SO_3Na/D_2O systems, the complete incorporation of deuterium allowed us to reject a direct SN2 substitution of CHF_2Cl by $SO_3^{=}$ and confirmed the following carbenic chain mechanism (Scheme III):

$$HO^{\ominus} + H\text{-}CF_2\text{-}Cl \longrightarrow H_2O + :CF_2 + Cl^{\ominus}$$

$$SO_3^{\ominus} + :CF_2 \longrightarrow {}^{\ominus}O\text{-}SO_2\text{-}CF_2^{\ominus}$$

$$^{\ominus}O\text{-}SO_2\text{-}CF_2^{\ominus} + D_2O \longrightarrow CDF_2\text{-}SO_3^{\ominus} + DO^{\ominus} \quad \text{major}$$

$$^{\ominus}O\text{-}SO_2\text{-}CF_2^{\ominus} + H_2O \longrightarrow CHF_2\text{-}SO_3^{\ominus} + HO^{\ominus} \quad \text{minor}$$

Scheme III

Another possible reprotonation reaction can be also rejected:

$$^{\ominus}O\text{-}SO_2\text{-}CF_2^{\ominus} + H\text{-}CF_2\text{-}Cl \longrightarrow CHF_2\text{-}SO_3^{\ominus} + :CF_2 + Cl^{\ominus}$$

Sodium diflate from dibromodifluoromethane

The above results prompted us to test if sulfite and hydroxyl anions were able to generate difluorocarbene from dibromodifluoromethane as do thiolates [20, 21]. Indeed, when an aqueous solution of sodium sulfite B and sodium hydroxide was reacted with CF_2Br_2, bromide, fluoride and diflate anions were formed with the exclusion of bromodifluoromethanesulfonate

$$CF_2Br_2 + Na_2SO_3 \xrightarrow[150°C/20\ h]{NaOH/H_2O} CHF_2SO_3Na + NaBr$$

R1= 30% R2= 33% R3= 18% R4= 19%

There was no doubt that a carbenic process was also involved:

$$Nu^{\ominus} + Br\text{-}CF_2\text{-}Br \longrightarrow Nu\text{-}Br + :CF_2 + Br^{\ominus} \quad Nu^{\ominus} = HO^{\ominus} \text{ or } SO_3^{\ominus}$$

$$SO_3^{\ominus} + :CF_2 \longrightarrow {}^{\ominus}O\text{-}SO_2\text{-}CF_2^{\ominus}$$

$$^{\ominus}O\text{-}SO_2\text{-}CF_2^{\ominus} + H_2O \longrightarrow CHF_2\text{-}SO_3^{\ominus} + HO^{\ominus}$$

Scheme IV

As CF_2Br_2 was proved to react better, in an halophilic attack, with soft anions than with hard [20], it was supposed that the nucleophile involved in the first equation of Scheme IV was preferably sulfite which was, consequently, partially consumed by this reaction. The values obtained for R1-R4 were in accord with this hypothesis which led to the two following global reactions:

$$CF_2Br_2 + 2\ SO_3^{\ominus} + HO^{\ominus} \longrightarrow CHF_2SO_3^{\ominus} + 2\ Br^{\ominus} + SO_4^{\ominus}$$

$$CF_2Br_2 + SO_3^{\ominus} + 4\ HO^{\ominus} \longrightarrow CO + 2\ F^{\ominus} + 2\ Br^{\ominus} + SO_4^{\ominus} + 2\ H_2O$$

Physical properties of sodium difluoromethanesulfonate

Sodium diflate was obtained as a stable monohydrate melting at 220°C and stable up to 330°C with only a slight loss of water. Recrystallization in acetone delivered a less hydrated form CHF_2SO_3Na, 0.3 H_2O. The solubility of the monohydrated compound in acetone at 20°C is 3.5g/100g.

CONCLUSION

This work demonstrates unambiguously that the formation of sodium difluoromethanesulfonate from chlorodifluoromethane and sodium sulfite involves a carbenic process which is dramatically improved by adding sodium hydroxide to deprotonate chlorodifluoromethane. This base should, theoretically, act as a catalyst but is partially consumed through side reactions. However, an optimum yield could be reached with less than the stoichiometric amount of sodium hydroxide. Provided that a suitable vessel material could be found, higher yields should be obtained by increasing the reaction temperature. Sodium difluoromethanesulfonate could also be formed from dibromodifluoromethane, sodium sulfite and sodium hydroxide through a carbenic process.

EXPERIMENTAL

Sodium sulfite and chlorodifluoromethane were commercially available and used without further purification. Sulfite A was purchased from Prolabo and sulfite B from Bietrix. Potassium sulfite was prepared according to [26]. ^{1}H , ^{19}F or ^{2}D NMR spectra were recorded, at 100 MHz, 93.65 MHz and 15.24 MHz respectively, on a Jeol FX 100 spectrometer (D_2O as solvent for ^{1}H and ^{19}F NMR and H_2O for ^{2}D NMR; Tetramethylsilane, trifluoroacetic acid and hexadeuteroacetone as standards respectively, positive ^{19}F and ^{2}D chemical shifts downfield from trifluoroacetic acid and hexadeuteroacetone). I.R. spectra were recorded on a Perkin-Elmer 457 spectrometer. Differential calorimetric analysis was performed on a Du Pont Instruments DSC 990 apparatus in a tight titanium cap. Chlorides or bromides were determined by a classical potentiometric technique on a Metrohm apparatus fitted with a silver electrode and fluorides on a Tacussel Isis 2000 potentiometer fitted with a specific Orion PF4 electrode (TISAB buffer). Water content was determined by Karl-Fischer titration.

Synthesis of sodium difluoromethanesulfonate from chlorodifluoromethane (entry 6)

In a 1 liter stainless steel pressure vessel, cooled with acetone and dry ice, were introduced 156.0 g (1.8 mole) of liquified CHF_2Cl (Eb= -40°C), 151.2 g (1.2 mole) of anhydrous sodium sulfite and 24.0 g (0.6 mole) sodium hydroxide dissolved in 500 ml of distilled water. When closed, the vessel was shaken while heating to 150°C. This temperature was maintained for 20 h and the autogeneous pressure reached 43 bars. After cooling and degassing, the reaction medium was evaporated to dryness under reduced pressure, and the residue extracted with acetone, in a Soxhlet apparatus. The organic phase was evaporated and gave pure monohydrated sodium difluoromethanesulfonate (0.612 mole) characterised by its NMR (^{1}H, ^{19}F) and IR spectra. The insoluble part contained sodium chloride (1.122 mole by argentimetric titration), sodium fluoride (0.867 mole by fluoride determination) and unconverted sodium sulfite. Carbon monoxide has been detected by a specific emergency apparatus.

Physical properties of sodium difluoromethanesulfonate

Infra-red spectrum (KBr, cm^{-1})

ν asym. S=O : 1250, 1230, 1210

ν sym. S=O : 1080, 1040

δ asym. O-S-O : 650

δ sym. O-S-O : 560, 530

OH (hydrated form): 3450 (large)

NMR spectra (D_2O solvent)

^{1}H NMR (TMS) δ = 6.4 ppm (t) $^{2}J_{HF}$= 53.7 Hz

^{19}F NMR (CF_3CO_2H) δ = -45.8 ppm (d)

Differential calorimetric analysis

Melting endotherm at 220°C.

Beginning of autocatalytic decomposition at 330°C.

Attempts to dehydrate sodium difluoromethanesulfonate

Thermogravimetric analysis of CHF_2SO_3Na,H_2O until 200°C under

atmospheric pressure indicated a slight continuous loss of water only. An overnight drying under reduced pressure dropped the hydration to CHF_2SO_3Na, 0.7 H_2O only and recrystallization in acetone to CHF_2SO_3Na, 0.3 H_2O.
Solubility of CHF_2SO_3Na,H_2O in acetone at 20°C= 3.5 g/100 g

Formation of sodium difluoromethanesulfonate from CF_2Br_2

The same procedure was performed (cf. entry 6) except that the vessel was cooled, before introducing the reagents, with an ice-NaCl bath. The following amounts were used: 37.8g (0.3 mole) anhydrous Na_2SO_3, 12.0g (0.3 mole) NaOH, 50 ml of water and 126.0g (0.6 mole) CF_2Br_2. Diflate yield= 19%

Synthesis of sodium deuterodifluoromethanesulfonate

The previously described procedure (entry 6) was performed in a 50 ml stainless steel pressure vessel fitted with an axial mechanical stirrer using 0.050 mole anhydrous sodium sulfite, 0.025 mole sodium hydroxide, 0.075 mole chlorodifluoromethane and 21 ml deuterium oxide. Work-up is the same as in the preceding example. ^1H, ^{19}F and ^2D NMR spectra of the obtained sulfonate were:

CHF_2SO_3Na
^1H NMR (TMS) δ= 6.4 ppm (1/2/1 triplet) $^2J_{HF}$= 53.7 Hz
^{19}F NMR (CF_3CO_2H) δ= -45.8 ppm (doublet)
CDF_2SO_3Na
^2D NMR (CF_3COCF_3) δ= 6.2 ppm (1/2/1 triplet) $^2J_{DF}$= 8.3 Hz
^{19}F NMR (CF_3CO_2H) δ= -46.4 ppm (1/1/1 triplet)

Integration of the ^{19}F NMR spectrum indicated that this salt contained 99.5 mole% CDF_2SO_3Na and 0.5 mole% CHF_2SO_3Na.

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REFERENCES

1 C. Wakselman and M. Tordeux, Eur. Pat. 165 135 (5/23/1984). Bull. Soc. Chim. Fr., (1986) 868.

2 M. Tordeux, B.R. Langlois and C. Wakselman, Fr. Demande 2 593 808 (1986).

3 B.R. Langlois, Eur. Pat. 28 964 (11/13/1979).

4 B.R. Langlois, Fr. Pat. 2 504 923 (4/29/1981).

5 Mitsui Toatsu Chemicals Inc., Fr. Pat. 2 150 486 (4/6/1973).

6 U.S. Sec. of Navy, U.S. Pat. 4 048 219 (9/13/1977); U.S. Pat. 4 062 897 (12/13/1977).

7 G.T. Brown and R.D. Bowden, Eur. Pat. 57 507 (1/29/1981).

8 Rhône-Poulenc Industr., Eur. Pat. 3 205 & 3 206 (7/25/1979).

9 N. Yoneda, T. Fukuhara and S. Nozawa, Ger. Offen. 3 542 481 (12/11/1984).

10 J.A. Daniels, Eur. Pat. 125 769 (4/18/1983).

11 J.B. Rose and M.B. Cinderey, Eur. Pat. 75 389 (9/17/1981).

12 J.B.Rose, Eur. Pat. 63 874 (4/29/1981).

13 Q.Y. Chen and S.Z. Zhu, Acta Chim. Sinica, 43 (1985) 546.

14 Q.Y. Chen and S.Z. Zhu, Acta Chim. Sinica, 44 (1986) 92.

15 Q.Y. Chen and S.Z. Zhu, Acta Chim. Sinica, 44 (1986) 812.

16 G.A. Sokolski and I.L. Knunyants, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1961) 1606; Chem. Abst. 56 7116g.

17 G.A. Sokolski, M.A. Belaventsev and L.I. Ragulin, USSR Pat. 189 842 (12/16/1966).

18 N.D. Volkov, V.P. Nazaretian and L.M. Yagupolskii, Synthesis, (1979) 972; Zh. Org. Khim., 13 (1977) 1788.

19 G.G.I. Moore, J. Org. Chem., 44 (1979) 1708.

20 I. Rico, 'Action de nucléophiles sur les perhaloalcanes BrCF2X (X=Br,Cl,CF2Br): intervention de différents processus en chaîne', Thesis, Paris VI, (06/03/1982).

21 I. Rico and C. Wakselman, Tetrahedron Lett., 1981 (22) 323.

22 R.F. Sweeney, J.O. Peterson, B. Sukornick, M.B. Berenbaum, H.R. Nychka and R.E. Eibeck, Can. Pat. 1 093 581 (1/13/1981).

23 W.V. Farrar, J. Chem. Soc., (1960) 3058

24 R.D. Chambers, in 'Fluorine in Organic Chemistry', Wiley, (1973).

25a J. Hine and J.J. Porter, J. Am. Chem. Soc., 79 (1957) 5493.

b J. Hine, in 'Divalent Carbon', Ronald Press N.Y. (1964), 39.

c J. Hine and P.B. Langford, J Am. Chem. Soc., 79 (1957) 5497.

d J. Hine and K. Tanabe, J. Am. Chem. Soc., 80 (1958) 3002.

e W. J. Lenoble, J. Am. Chem. Soc., 87 (1965) 2434.

26 H.F. Johnstone, Inorg. Syntheses, vol. II, 162, McGraw-Hill, New York (1946).