Journal of Fluorine Chemistry, *23* (1983) 193–204

Received: November 29, 1982; accepted: April 11, 1983

STUDIES ON DEIODO-SULFINATION. PART I. STUDIES ON THE DEIODO-SULFINATION OF PERFLUOROALKYL IODIDES[*]

WEI-YUAN HUANG, BING-NAN HUANG and CHANG-MING HU

Shanghai Institute of Organic Chemistry, Academia Sinica
345 Lingling Lu Shanghai 200032 (China)

SUMMARY

The normal reaction products of 5-iodo-3-oxaoctafluoropentanesulfonyl fluoride (I) with K_2SO_3 in aqueous solution are potassium 5-iodo-3-oxaoctafluoropentanesulfinate (II) and 5-H-3-oxaoctafluoropentanesulfinate (III), but when the reaction is carried out in aqueous dioxane potassium 3-oxaoctafluoropentane-1,5-disulfinate (IV) is formed in high yield accompanied by a very very small amount of III. 7-Iodo-3-oxadodecafluoroheptanesulfonyl fluoride (IX) and 1,4-diiodo-octafluorobutane (X) are similarly converted into the corresponding disulfinates VII and VIII respectively. The name, deiodo-sulfination, is suggested for the conversion of R_FI to R_FSO_2K in one step. The reaction can also be carried out in diglyme or THF but not in N-methylmorpholine, pyridine or triethylamine.

The effect of light, reaction temperature, radical inhibitor, single electron scavenger, peroxide and the nature of the solvents are studied, and a radical chain mechanism involving a single electron transfer process is proposed.

---

[*] Preliminary communication: Huang Bing-nan, Huang Wei-yuan and Hu Chang-ming, Acta Chimica Sinica 39 481 (1981)

INTRODUCTION

In our laboratory it was found that the group -CF_2I of some perfluoroalkyl iodides reacted with potassium sulfite in aqueous dioxane[**] to yield -CF_2SO_2K in one step. We suggest that this previously unreported reaction be called "deiodo-sulfination". Previously the transformation was only achieved via the reaction of the corresponding organometallic compounds with sulfur dioxide (1) (2).

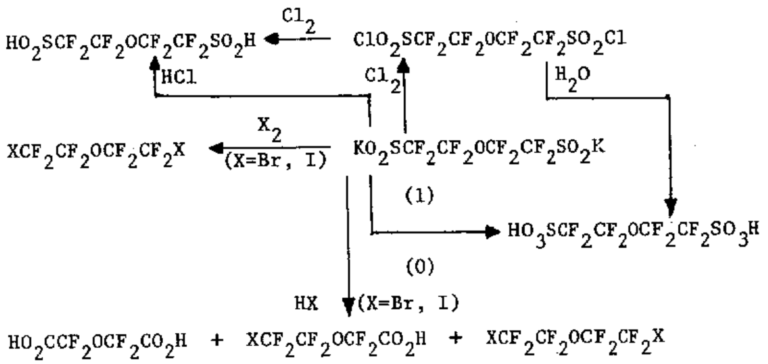
RESULTS AND DISCUSSION

The reaction products of 5-iodo-3-oxaoctafluoropentanesulfonyl fluoride (I) with potassium sulfite in aqueous solution were potassium 5-iodo-3-oxaoctafluoropentanesulfinate (II) and potassium 5-H-3-oxaoctafluoropentanesulfinate (III) (II : III = 3 : 1) (3). However, a different reaction took place in aqueous dioxane to give potassium 3-oxa-octafluoropentane-1.5-disulfinate (IV) instead of II as the main product, the by-product III was only produced in a very small amount. In this latter reaction the -SO_2F group in I was converted to -SO_2K in the usual manner, however, the -CF_2I group in I underwent a new reaction and was converted to -CF_2SO_2K. Similarly, sodium 3-oxaoctafluoropentane-1.5-disulfinate (V) was obtained when sodium sulfite was employed as the reagent. The yields were 85-90%:

$$\underset{(I)}{ICF_2CF_2OCF_2CF_2SO_2F} + M_2SO_3 \xrightarrow[\text{dioxane}]{H_2O} \underset{(IV)\ (M=K);\ (V)\ (M=Na)}{MO_2SCF_2CF_2OCF_2CF_2SO_2M} + III$$

IV forms colorless crystals with a sharp melting point. It is stable to water, alcohol and mineral acids and soluble in many polar solvents such as alcohol, acetonitrile, ethyl acetate. The ^{19}F NMR spectrum shows equal intensity two singlets at 82.0, 133.4 ppm. The results of elemental analysis and redox titration agreed with the structure of IV. That the transformation products of IV showed the expected symmetrical structures except $XCF_2CF_2OCF_2CO_2H$ further confirmed our conclusion (10) (See Scheme 1).

[**] Dioxane mentioned in this paper contained about 0.5% (by weight) peroxide unless specified otherwise



Scheme 1

When the molar ratio of reducing agent to I was larger than 3, a complete deiodosulfination was achieved, the yield of IV was as high as 90%. When the ratio was below 2, the yield of IV was lower and II was formed as the main product, apparently because the rate of deiodosulfination was slower than that of the reduction of sulfonyl fluoride group to sulfinate. It was found that deiodosulfination was very slow below 50°C, however, above 90°C the yield of IV also decreased slightly due to the evolution of sulfur dioxide and the oxidation of the potassium sulfinate to the corresponding sulfonate as detected from the ^{19}F NMR spectrum. Thus the optimal reaction temperature range lies between 70°C and 85°C. A suitable solvent volume ratio was dioxane : water = 1 : 2-3 and the reaction can be carried out in ordinary glassware.

Besides dioxane, other ether-type solvents such as diglyme and THF can also be used. The deiodosulfination reaction does not take place in pyridine, triethylamine or N-methyl-morpholine, however, in these solvents the reduction of -CF_2I to -CF_2H was accelerated. For example, the predominant product was potassium 5-H-3-oxaoctafluoropentanesulfonate (VI) (85% yield), when I was reacted with K_2SO_3 in aqueous N-methylmorpholine, indicating the -SO_2F group underwent hydrolysis much faster than reduction under these circumstances.

In a similar way, potassium 3-oxadodecafluoroheptane-1.7-disulfinate (VII) (80%) and potassium octafluorobutane-1.4-disulfinate (VIII) (8%)[***] were obtained from 7-iodo-3-oxadodecafluoroheptanesulfonyl fluoride (IX) and 1.4-diiodooctafluorobutane (X) respectively.

[***] The low yield of VIII is probably due to the poor solubility of X in aqueous dioxane

That an alkyl iodide reacted with sodium sulfite to give the corresponding sulfonate was a well-known process. However, it was proved that the sulfonate was not an intermediate of deiodo-sulfination reaction by the fact that attempted conversion of VI to the corresponding sulfinate under the deiodo-sulfination conditions failed, and only the starting material was recovered.

Apparently, the deiodo-sulfination reaction involved the formation of a C-S bond with the cleavage of a C-I bond and a S-O bond. It is interesting to investigate the nature of this reaction in order to shed some light on the reaction mechanism.

The presence of a small amount (1-2% by weight) of an inhibitor such as hydroquinone was enough to suppress the deiodo-sulfination as well as the reduction of $-CF_2I$ to $-CF_2H$ in I and IX. The results implied the free radical nature of these two transformations;

$$\underset{\text{(I) (n=1); (IX) (n=2)}}{I(CF_2CF_2)_nOCF_2CF_2SO_2F} + K_2SO_3 \xrightarrow[\text{1-2\% hydroquinone}]{\text{water dioxane}} \underset{\text{(II) (n=1); (XI) (n=2)}}{\underset{80\text{-}85\%}{I(CF_2CF_2)_nOCF_2CF_2SO_2K}}$$

Addition of electron scavengers (4), (5) e.g. p-dinitrobenzene (1-2% by weight) to the reaction system also block deiodo-sulfination, but the free radical reduction of $-CF_2I$ to CF_2H was not disturbed:

$$\text{I} + K_2SO_3 \xrightarrow[\text{1-2\% p-dinitrobenzene}]{\text{water, dioxane}} \text{II} + \text{III}$$

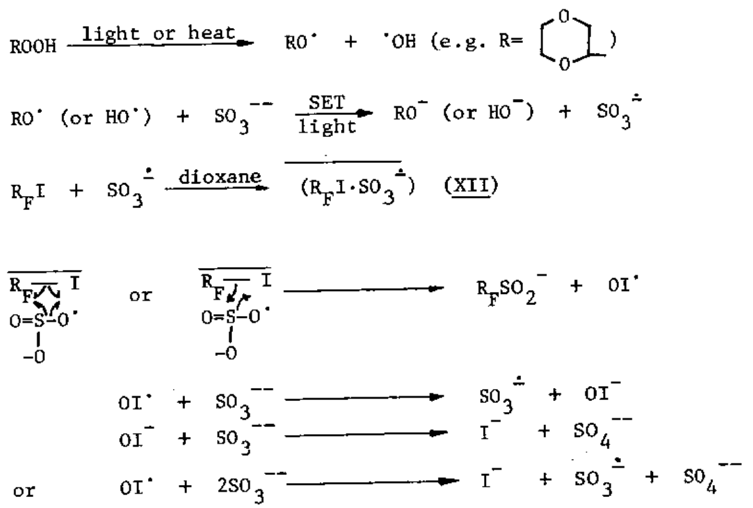
$$\text{II} : \text{III} \simeq 4 : 1$$

The presence of light is essential for deiodo-sulfination. In the dark I gave only II and III in place of the anticipated IV under deiodo-sulfination conditions. Diffused indoor light was enough to bring about this reaction to give IV as the final product.

Furthermore, the concentration of peroxide in dioxane plays an important role in the reaction of $-CF_2I$ group of compound I. No deiodo-sulfination was detected in peroxide-free dioxane and the conversion of $-CF_2I$ to $-CF_2H$ was also supressed. For instance, without dioxane, I reacted with aqueous K_2SO_3 solution to form not only II but also 22% of III (3). On adding peroxide-free dioxane to the reaction mixture the products were still II and III, but the yield of III dropped to below 2%. A small amount (ca. 0.5% by weight) of peroxide is essential for the deiodo-sulfination of I. Interestingly, no IV was obtained when the peroxide content was too high (for example, over 10%). Under such condition the reduction of $-CF_2I$ to $-CF_2H$ became the main reaction and III was obtained in over 80% yield. The addition of azobisisobutyronitrile to the reaction mixture of I, K_2SO_3, water and peroxide-free dioxane also caused reduction of $-CF_2I$ to $-CF_2H$ but not deiodo-sulfination, thus :

$$\text{I} + K_2SO_3 \xrightarrow[\text{2-3\% AIBN}]{\text{water peroxide-free dioxane}} \underset{80\%}{HCF_2CF_2OCF_2CF_2SO_2K}\ \text{(III)}$$

The results mentioned above as well as the appearance of a characteristic bright yellow coloration during deiodo-sulfination suggested that this novel reaction might involve a single electron transfer free-radical chain process. A mechanism is tentatively proposed to account for all the experimental results (See Scheme 2):



Scheme 2

Similar to changes in U.V. spectra of perfluoroalkyl iodides in solution (6), ^{19}F NMR spectroscopy shows that the chemical shift of $-CF_2I$ in I shifted markedly to lower field on mixing with solvents containing unshared electron pairs (Table 1).

TABLE 1.

Solvent effect on ^{19}F NMR chemical shift of $-CF_2I$ in I

Solvents used	Dioxane	Diglyme	THF	DMF	DMSO	N-Methyl-morpholine	Pyridine	Triethyl-amine
δ_s	68.7	69.4	69.6	71.3	72.5	75.4	75.5	76.5
$\Delta\delta=\delta_s-\delta_o$	3.7	4.4	4.6	6.3	7.5	10.4	10.5	11.5
DN	14.8	(19.0)	20.1	26.6	29.8	(32.9)	33.1	34.6

The molar ratios of I to solvent used were 1:1

δ_o, δ_s were the chemical shifts of $-CF_2I$ in neat I and in solution respectively. δ_o=65.0 ppm

The values in brackets were estimated from Fig. 1

It was suggested by Gutmann (7) that the donicity of an unshared electron pair can be expressed by the value of Donor Number (DN). A roughly straight line was obtained when the logarithms of differences of chemical shifts ($\Delta\delta$) were ploted against DN. The higher the DN, the larger the difference of chemical shift and the stronger the donor-acceptor action (Fig. 1)

The donor-acceptor action between solvent and the substrate enhances the polarization of the C-I bond in R_FI through the dispersion of the positive charge on the iodine atom. In the extreme case, a strong donor-acceptor effect between solvent and positively polarized iodine atom of R_FI might facilitate the heterolytic cleavage of C-I bond. The conversion of $-CF_2I$ in I to $-CF_2H$ in aqueous N-methylmorpholine probably belonged to this category. In these reacting systems, the addition of hydroquinone did not stop the formation of VI at all. However, the DN values of dioxane, diglyme, THF were not large enough to cause the heterolysis of the C-I bond, but these ether-type solvents might form a solvent cage around the complex XII and promoted the kind of bond cleavage resulting in deiodo-sulfination.

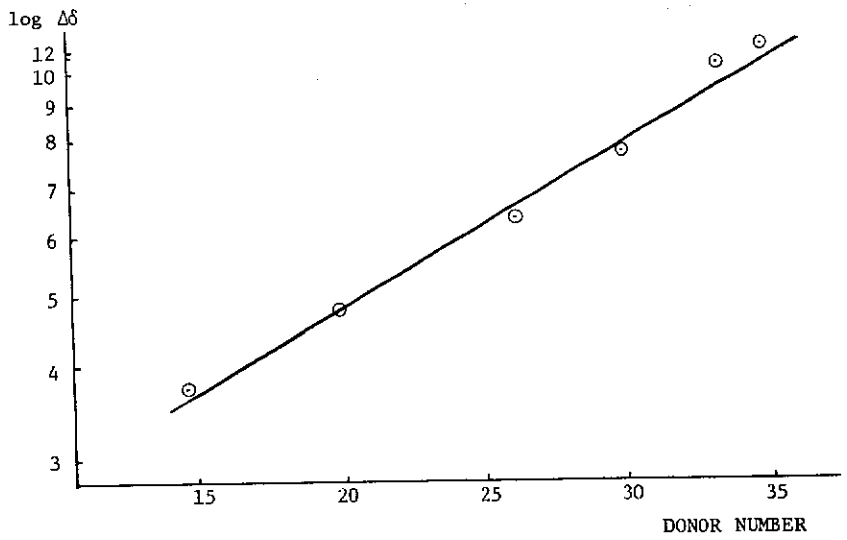


Fig. 1. Plot of log $\Delta\delta$ vs. DN

EXPERIMENTAL

All melting points were uncorrected. NMR spectra were taken on a Varian XL-200 NMR spectrometer at 200 MHz and EM-360 NMR spectrometer at 60 MHz using TFA as external standard and δ $CFCl_3$(positive upfield) was calculated by δ $CFCl_3$=δ CF_3CO_2H + 76.8. Infrared spectra were measured on a Carl Zeiss Specord 75 IR spectrometer using NaCl windows

Potassium 3-oxaoctafluoropentane-1,5-disulfinate (IV)

In a 250 ml three necked round-bottomed flask were placed 88 g (0.21 mole) compound I, 108 g (0.68 mole) anhydrous potassium sulfite, 90 ml water and 30 ml dioxane. Under a stream of nitrogen the contents were stirred vigorously at 75-80°C for 8 hrs. After removal of solvents the residue was mixed with 260 ml of boiling isopropanol with stirring and then filtered while hot. The filtrate was evaporated to dryness in rotary evaporator under nitrogen to give 88 g of white solid, which was crystallised from isopropanol to yield IV 82 g (86% yield). Pure IV (nc) forms colorless needles, m.p. 236-237°C and is very hygroscopic.

Analysis : Calculated for $C_4F_8K_2O_5S_2 \cdot 2H_2O$, C, 10.48; H, 0.88; F, 33.16; K, 17.05; S, 13.96% Found : C, 10.23, 10.08; H, 0.47, 0.42; F, 32.28, 32.20; K, 16.23, 16.30; S, 13.51. 13.61%

IR (KCl) : 1010 (S-O), around 1200 (vs, C-F) cm^{-1} (these peaks appear in all the compounds). IR (perfluorinated nujol) : 3400 (broad O-H) cm^{-1} (this peak also appears in all the following compounds).

^{19}F NMR (methanol) : δ =82.0 (s, OCF_2) 133.4 (s, CF_2SO_2K) ppm, of equal intensity.

Sodium 3-oxaoctafluoropentane-1,5-disulfinate (V)

A mixture of 22 g (0.052 mole) I, 24 g (0.19 mole) anhydrous sodium sulfite, 20 ml water and 8 ml dioxane were allowed to react in a similar way to give 24 g of white solid. The crude product was extracted with hot ethyl acetate and compound V (nc) was obtained as a white hygroscopic powder (18.9 g, 85% yield)

IR (KCl) : 1010 (S-O) cm^{-1}

^{19}F NMR (methanol) : δ=81.0 (s, OCF_2); 131.6 (s, CF_2SO_2Na) ppm, of equal intensity.

Potassium 5-H-3-oxaoctafluoropentanesulfonate (VI)

A mixture of 7.0 g (16 mmol) I, 8.0 g (51 mmole) anhydrous potassium sulfite, 7 ml water and 2.5 ml N-methylmorpholine was allowed to react at 80°C for 8 hrs. Extraction with isopropanol gave a white solid 5.7 g (85% yield). Recrystallisation from water afforded colorless tabular crystals. m.p. 252-254°C. (nc)

Analysis : Calculated for $C_4HF_8KO_4S \cdot H_2O$, C, 13.56; H, 0.85; S, 9.05; F, 42.91; Found : C, 13.98, 14.20; H, 1.09, 1.24; S, 8.80, 8.75; F, 42.90, 42.73%

IR (KCl) : 1066 (S-O) cm^{-1}.

^{19}F NMR (methanol) : δ = 138.2 (d-t, HCF_2), 88.8 (t-t, CF_2O), 81.5 (t-t, OCF_2), 117.6 (t, CF_2SO_3K) ppm, all of the same intensity.

The corresponding sulfonic acid had the same ^{19}F NMR spectrum as a known sample (9).

^{19}F NMR (neat) : δ = 138.0 (d-t, HCF_2), 89.5 (t-t, OCF_2), 82.9 (t-t, OCF_2), 117.9 (t, CF_2SO_3H) ppm, all of the same intensity.

Potassium 3-oxadodecafluoroheptane-1,7-disulfinate (VII)

In a similar manner, the reaction product from a mixture of 8.6 g (16 mmole) IX, 7.8 g (49 mmole) anhydrous potassium sulfite, 7 ml water and 2.5 ml dioxane on recrystallisation from azeotropic isopropanol gave 7.5 g of colorless needles (81% yield). m.p. 241-242°C (nc) (decomposed).

Analysis : Calculated for $C_6F_{12}K_2O_5S_2 \cdot H_2O$: C, 13.34; H, 0.37; S, 11.86; F, 42.18%. Found : C, 13.22, 13.16; H, 0.32, 0.42; S, 11.48, 11.48; F, 42.88, 42.67%

IR(KCl) : 1010 (S-O) cm^{-1}.

^{19}F NMR (methanol) : δ = 133.1, 130.0 (both, s, CF_2SO_2K), 129.6 123.6 (both, s, CF_2), 82.0, 81.6 (both, s, OCF_2) ppm, all of equal intensity.

Attempted reduction of potassium 5-H-3-oxaoctafluoropentane sulfonate (VI)

2.5 g (7.1 mmole) VI, 3.0 g (19 mmole) anhydrous potassium sulfite, 4 ml water and 1.5 ml dioxane were stirred at 75-80°C for 8 hrs. and 2.5 g of white solid was isolated, which was shown by IR and ^{19}F NMR (methanol) spectra to be the unchanged starting material.

The deiodo-sulfination of compound I in diglyme

3.5 g (8.2 mmole) I, 4.0 g (25 mmole) anhydrous potassium sulfite, 3.5 ml water and 1.5 ml diglyme were heated to 80-85°C for 9 hrs. to give 3.5 g of a white solid, which was shown by ^{19}F NMR spectroscopy to contain IV and III in a ratio of ca. 2.5:1.

^{19}F NMR of III (methanol) : δ=137.6 (d-t, HCF_2), 83.0, 82.0 (t-t, each CF_2O), 133.1 (t, CF_2SO_2K) ppm, all of the same intensity.

III was further characterized by converting to the corresponding sulfonyl chloride (10).

The deiodo-sulfination of 1,4-diiodo-octafluorobutane (X)

9.8 g (20 mmole) X, 25.4 g (161 mmole) anhydrous potassium sulfite, 22 ml water and 7.5 ml dioxane were allowed to stir at around 80°C for 15 hrs. The crude product was recrystallised from acetonitrile several times to afford white feather-like crystals (VIII) (0.98 g, 8% yield) m.p. 228-230°C (decomposed) (nc)

Analysis : Calculated for $C_4F_8K_2O_4S_2 \cdot 2H_2O$: C, 10.86; H. 0.91; F, 34.36; S, 14.49; Found : C, 11.10, 11.32; H, 0.89, 0.72 F, 35.02, 35.05; S, 14.68, 14.83%.

IR (KCl) : 1010 (S-O) cm^{-1}.

^{19}F NMR (methanol) : δ = 132.8 (s, CF_2SO_2K), 117.4 (s, CF_2CF_2)ppm. of equal intensity.

The effect of light on the deiodo-sulfination of I

A mixture of 7.0 g (16.4 mmole) I, 8.0 g (51 mmole) anhydrous potassium sulfite, 7 ml water and 2.5 ml dioxane was allowed to react in the dark at 80°C for 8 hrs. to give 7.1 g of a white solid, which was shown by ^{19}F NMR spectroscopy of its corresponding sulfinic acid to be compound II.

The inhibitory effect of hydroquinone on the deiodo-sulfination of I

7.0 g (16 mmole) I, 8.0 g (51 mmole) anhydrous potassium sulfite, 7 ml water, 2.5 ml dioxane and 0.15 g (2.1% of I by weight) hydroquinone were subjected to react at 80°C for 8 hrs. Isolation gave 6.5 g of a white solid (85% yield), which was shown by ^{19}F NMR spectrum to be compound II contaminated with only a very small amount of III.

The inhibitory effect of hydroquinone on the deiodo-sulfination of IX

8.6 g (16 mmole) IX, 8.0 g (51 mmole) anhydrous potassium sulfite, 9 ml water, 3 ml dioxane and 0.12 g (2.1% of IX by weight) hydroquinone were heated to 80°C for 9 hrs. to give 6.5 g of a white solid XI contaminated with ca. 1% of the corresponding omega-H-compound (83% yield).

IR of XI (KCl) : 1010 (S-O) cm^{-1}.

^{19}F NMR (methanol) : δ = 65.0 (s, ICF_2), 112.9, 123.6 (s, each CF_2), 82.0, 81.6 (both, s, OCF_2), 130.0 (s, CF_2SO_2K) ppm, all of the same intensity.

Compound XI was further characterized by converting to 7-iodo-3-oxadecafluoroheptanoic acid (XIII) (10).

The inhibitory effect of p-dinitrobenzene on the deiodo-sulfination of I

A mixture of 7.0 g (16 mmole) I, 8.0 g (51 mmole) anhydrous potassium sulfite, 7 ml water, 2.5 ml dioxane and 0.11 g (1.6% of I by weight) p-dinitrobenzene was stirred at 80°C for 8 hrs. The ^{19}F NMR spectrum of the reaction product showed that II and III were produced in a molar ratio of ca. 4:1.

The effect of hydroquinone on the reaction of compound I with K_2SO_3 in aqueous N-methylmorpholine

3.5 g (8.2 mmole) I, 4.0 g (25 mmole) anhydrous potassium sulfite, 4 ml water, 1.8 ml N-methylmorpholine and 0.5 g hydroquinone (14.3% of I by weight) were allowed to react at 80°C for 9 hrs. The product isolated was shown by ^{19}F NMR spectroscopy to be predominantly VI.

The effect of peroxide concentration on the deiodo-sulfination reaction of I in dioxane

3.5 g (8.2 mmole) I, 4.0 g (25 mmole) anhydrous potassium sulfite, 3.5 ml water and 1.5 ml peroxide-free dioxane were heated to ca. 80°C for 8 hrs. The white solid 3.2 g isolated was shown by ^{19}F NMR spectroscopy to be mainly II contaminated with a very small amount of III.

If 1.5 ml dioxane containing over 11% peroxide was used in place of the peroxide-free dioxane in the same reaction mixture as shown above, the product, 2.2 g white solid (80% yield), was a mixture of III and II in molar ratio of ca. 3:1

Preparation of dioxane containing peroxide

Peroxide containing (5-10%) dioxane was prepared according to the literature procedure and analysed by iodometric method (11).

ACKNOWLEDGEMENT

We would like to thank Professor Jiang Xi-Kui for his helpful discussion about the reaction mechanism.

REFERENCES

1 A. Commeyras, H. Blancou and A. Lantz, Ger. Offen 2,756,169 (1978) Chem. Abstr. 89 108,161e

2 K. Von Werner and H. Blank, Angew. Chem. 92 124 (1980)

3 Huang Wei-yuan,Huang Bing-nan and Hu Chang-ming, J.Fluorine Chem.23 229(1983)

4 A. H. Maki and D. H. Geske, J. Amer. Chem. Soc., 83 1852 (1961)

5 N. Kornblum: Angew. Chem. (Int. Ed.) 14 734 (1975)

6 R. N. Haszeldine, J. Chem. Soc. 2622 (1953)

7 V. Gutmann: The Donor-acceptor Approach to Molecular Interactions, New York, Plenum Press p20 (1978)

8 B. Haley, R. N. Haszeldine, B. Hewitson and A. E. Tipping: J. Chem. Soc., Perkin Trans., I 525 (1976)

9 Chen Qing-yun and Zhu Shi-zheng, Acta Chimica Sinica. in press

10 Huang Wei-yuan, Huang Bing-nan and Hu Chang-ming, to be published (Study on Deiodosulfination part II.)

11 E. K. Varfolomeeva and Z. G. Zolotova, Ukrain, Khim. Zhur. 25 708 (1959)