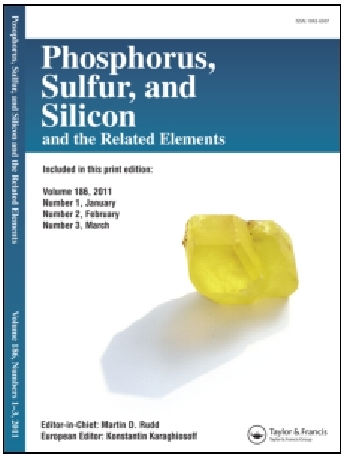

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OXIDATION OF SULFIDES BY IODYLARENES IN THE PRESENCE OF VANADYL ACETYLACETONATE AS A CATALYST

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Key words: Sulfide oxidation; sulfoxide; iodylarene; vanadyl acetylacetonate.

Iodylbenzene is a poor oxidant of sulfur, but in the presence of vanadyl acetylacetonate, sulfides are converted into sulfoxides, sulfones and S-dealkylated products. To improve the selectivity and the yield of this reaction, different substituted iodylarenes are used. The N-(paraiodylphenyl) palmitoylamid is a promising oxidant for synthetic purposes.

INTRODUCTION

Numerous methods have been developed for the transformation of sulfides to sulfoxides, utilizing reagents such as nitric acid,[1] hydrogen peroxide,[2] dinitrogen tetroxide,[3] chromic acid,[4] ozone,[5] peracids,[6] hydroperoxides,[7] sodium perborate,[8] selenonic acids,[9] sodium periodate.[10] Polyvalent iodine compounds (bis acetoxyiodobenzene,[11] iodosylbenzene[12]) are useful reagents for this reaction. We found that iodosylbenzene in methanol oxidised vinylsulfides to vinylsulfoxides at room temperature.[13] The chemistry of iodylbenzene ($C_6H_5IO_2$) has not been very explored, the interest in its use as oxidant for organic synthesis is relatively recent. Iodyl arenes are very poor oxidants but Barton has shown that an electrophilic complexation of the highly polarised iodine–oxygen bound reduced the kinetic activation barrier.[14] We described iodylbenzene vanadyl acetylacetonate system oxidised sulfides to sulfoxides, sulfones and S-dealkylated products.[15]

In this paper, in order to gain more information about the nature of the mechanism, we study the oxidation with substituted phenyl methyl sulfides and we improve this reaction in order to reach synthetic ways for the sulfoxides.

RESULT AND DISCUSSION

The oxidation of substituted thioanisoles ($XC_6H_4SCH_2R$) was performed by iodylbenzene (1 equivalent) in the presence of a catalytic amount of vanadyl acetylacetonate (0.012 equivalent). The heterogeneous mixture was stirred under reflux in dry benzene.

TABLE I

Oxidation of substituted thioanisoles by $C_6H_5IO_2$–$VO(acac)_2$

$XC_6H_4SCH_2R$ X	 R	Sulfide Yield (%)*	Sulfoxide Yield (%)*	Sulfone Yield (%)*	$(XC_6H_4–S)_2$ Yield (%)*
H	H	0	42	31	24
CH_3	H	8	36	50	3
F	H	1	32	60	10
Cl	H	31	60	10	0
Br	H	6	45	44	5
NO_2	H	14	72	14	0
H	C_6H_5	47	44	0	7
H	CO_2CH_3	37	48	6	17
H	$COCH_3$	10	56	16	7
H	CN	47	44	0	35
H	COC_6H_5	48	12	0	

* The yields were based on sulfide.

The results clearly demonstrated that iodylbenzene–$VO(acac)_2$ mixture was indeed an effective reagent for the transformations studied (Table I).

The S-oxygenation selectivity was increased by electron-withdrawing groups. A Hammett type correlation for the oxidation of $XC_6H_4SCH_3$ ($X = H$, F, Cl, Br, CH_3) between $\log k_X/k_H$ and σ^+ was observed. A linear relationship between electronic density on the sulfur atom computed by $CNDO_2$ and S-oxidation selectivity for $XC_6H_4SCH_2$—R ($X = H$, Cl, F and $R = H$, $COCH_3$, CN) was obtained. Kinetic isotopic effects, i.e. k_H/k_D of 3.8 and 3.1, have been found for thioanisole and phenacyl phenyl sulfide. All these results were in agreement with an electrophilic oxidising agent.

When we used sulfoxide as substrate, sulfone was obtained but the reaction was considerably slower with sulfoxide than the corresponding sulfide and the yield fell (Table II).

The insolubility in non polar solvents of iodylarenes could be an important factor of the weak oxidative power of these compounds. When we used iodyl-3 benzoic acid instead of iodylbenzene, a better selectivity in S-oxygenation (sulfoxide and sulfone) was observed (0.98 versus 0.75), but the yield of oxidation decreased (51% instead of 97%). Iodyl-3 toluene led to a good selectivity (92%) and a good yield (84%) but the sulfoxide was overoxidised in sulfone (20%). All the other oxidants (metafluoroiodylbenzene, tertio butyl-4 iodylbenzene and nitro-2 iodylbenzene) did not improve the reaction (Table III).

TABLE II

Oxidation of sulfoxides by $C_6H_5IO_2$–$VO(acac)_2$

$XC_6H_4SOCH_2R$ X	 R	Sulfoxide Yield (%)*	Sulfone Yield (%)*
H	H	30	64
CH_3	H	34	70
F	H	72	26
Cl	H	79	20
Br	H	71	30
H	CO_2CH_3	59	35

* The yields were based on sulfoxide

TABLE III

Oxidation of thioanisole by different iodylarenes in the presence of $VO(acac)_2$

Iodylarene	Conditions** (min, °C)		$C_6H_5SCH_3$ Yield (%)*	$C_6H_5SOCH_3$ Yield (%)*	$C_6H_5SO_2CH_3$ Yield (%)*	$(C_6H_5S)_2$ Yield (%)*
iodyl-3 benzoic acid	240	80	45	45	5	1
iodyl-3 toluene	360	80	7	64	20	0
fluoro-3 iodylbenzene	360	80	10	45	27	8
tertiobutyl-4 iodylbenzene	360	80	13	59	15	8
nitro-2 iodylbenzene	360	80	4	29	58	8
iodyl-4 phenyl	60	80	0	75	20	5
palmitate **1**	120	10	65	24	12	0
octyl iodyl-3	60	80	0	70	27	5
benzoate **2**	120	10	10	74	19	0
N-(iodyl-4 phenyl)	30	80	0	0	100	0
palmitoylamid **3**	120	10	0	91	0	0

* The yields were based on sulfide.

** These numbers are reaction time (min) and reaction temperature (°C), respectively.

Thus, we synthetized long chain substituted iodylarenes in the hope of enhancing the solubility of the oxidant agent. With para iodylphenylpalmitate **1**, octyl metaiodylbenzoate **2** and N-(para iodylphenyl) palmitoylamid **3**, thioanisole was consumed at 80°C within a 0.5 to 1 hour period. These compounds were active even at 10°C (Table III). The iodylarene **3** was the most attractive reagent: this oxidant led to sulfone at 80°C and to sulfoxide at 10°C. This excellent selectivity seems to be very promising for synthetic purposes.

EXPERIMENTAL

0.250 mmole of sulfide, 0.003 mmole of $VO(acac)_2$ in benzene (5 cm^3) were refluxed with 0.250 mmole of iodylarene. The reactions were monitoring by GPC (Perkin-Elmer 8310, Column: OV 17), the compounds were identified by gas chromatography-mass spectroscopy and comparison with pure samples.

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