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Organic Compounds of Polyvalent Iodine-Derivatives of Iodosobenzene

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The review describes the latest advances in the chemistry of aliphatic and aromatic iodoso-compounds, iodosohalides, iodosocarboxylates, and the derivatives of μ-oxobisacyloxy(aryl)iodine. A separate section is devoted to polymers with tervalent iodine.
The bibliography includes 300 references.

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I. INTRODUCTION

Having passed chlorine through a solution of iodobenzene in chloroform in 1886, Willgerodt[1,2] obtained, instead of the expected substitution product, the addition product $PhICl_2$, which was called phenyl iodosochloride in accordance with one of the then current nomenclatures. During the period which has elapsed since then, a wide variety of organic compounds containing iodine in the tervalent or quinquevalent state have been synthesised and their chemical properties have been investigated.

During the 1950's–1960's extensive studies were carried out on iodonium salts by Beringer in the USA and Nesmeyanov, Vanags, and Neilands in the USSR. Since the 1970's, the chemistry of aryl iodosocarboxylates has been developing successfully as a result of the efforts of scientists from many countries.

Despite the fact that the number of publications on the chemistry of organic compounds of polyvalent iodine is relatively small, nevertheless they have been covered in chronological order by fairly large numbers of periodically published reviews. The studies up to 1914 have been described in Willgerodt's monograph,[3] those published up to 1942 are dealt with in Sandin's review[2] already mentioned, and the studies up to 1965 are surveyed in Banks's review.[4] The data on all organic compounds of polyvalent iodine known up to 1955 are presented in the form of Tables in the review by Beringer and Gindler.[5] At the present time this field of chemistry has developed so widely that it is not possible to describe its present state in a single journal publication. There exists a brief review on iodonium salts[6] and one of the chapters of a monograph[7] is devoted to organic compounds of polyvalent iodine—mainly iodonium salts. The chemistry of aryl iodosocarboxylates is dealt with in a recently published review[8] and their application as oxidants is described in a monograph.[9] A review[10] is devoted to the use of polyvalent iodine compounds (mainly organic compounds) in organic chemistry. Interesting data on the chemistry of iodonium salts can be found also in other communications[11,12] and information about the chemistry of aryl iodosocarboxylates is available in books.[13,14]

The majority of organic compounds of polyvalent iodine belong to one of three large groups: the iodonium salts $R_2I^+X^-$, the iodonium ylides $R-\overset{+}{I}-\overline{E}$ (E = C or N), and derivatives of iodosobenzene PIY_2 (Y_2 = O or Y = Cl, F, or RCO_2).† The present review is devoted to the last group of compounds. The relation between various organic compounds of polyvalent iodine is illustrated in Scheme 1 for phenyl derivatives.

II. IODOSO-COMPOUNDS

1. Synthesis

Usually only the iodoso-derivatives of aromatic and heteroaromatic compounds and to a lesser extent vinyliodoso-compounds are relatively stable.[2] Among derivatives containing an iodine atom linked to an sp^3-carbon atom, only perfluoroalkyliodoso-derivatives are stable.

The iodoso-group can be introduced into certain arenes with electron-accepting substituents using the reaction of the latter with iodosyl sulphate:[16,17]

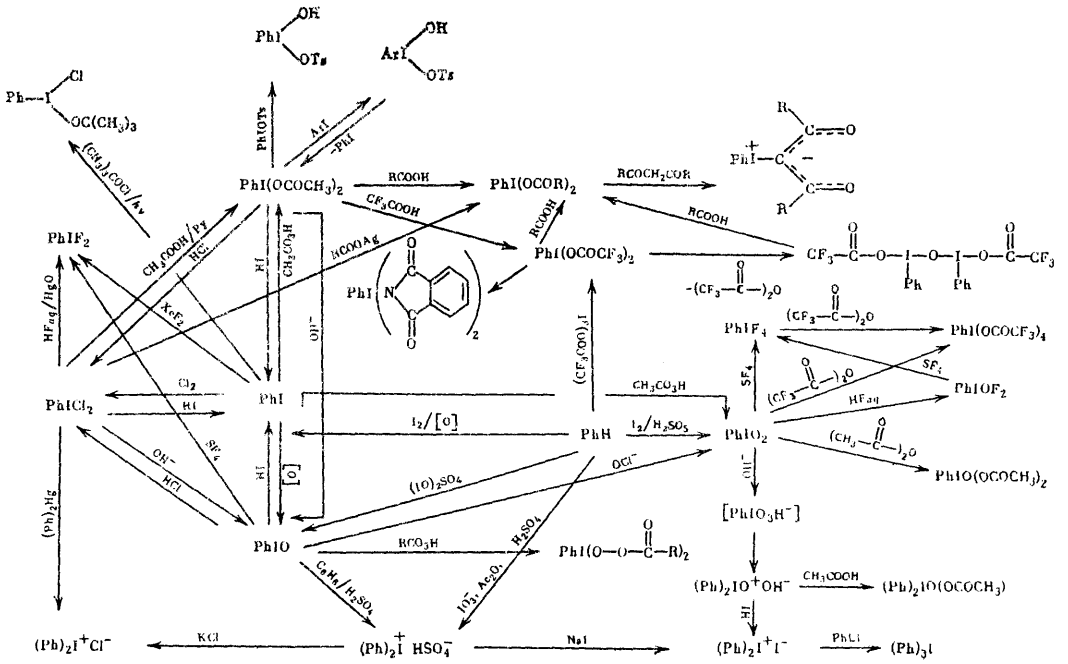
$$ArH \xrightarrow{(IO)_2SO_4/H_2SO_4} ArIO$$

Among the methods based on the hydrolysis of phenyl iodosochloride or phenyl iodosoacetate,[18,19] preference should be given to the latter because it is less laborious and the initial compound is stable on storage. Iodosobenzene can be prepared by the reaction of phenyl iodosochloride with silver oxalate, carbonate, or nitrate in acetonitrile.[20]

A number of specific methods for the synthesis of perfluoroalkyliodoso-derivatives have been proposed—for example the ozonolysis of perfluoroiodoalkanes,[21] the hydrolysis of the trifluoroacetates of iodosoperfluoroalkanes,[22] or

†The existence of iodosobenzene in the polymeric form $(PhIO)_n$ has been reported.[15]

Scheme 1



the interaction of perfluoroalkyl iodosofluorides with silicon dioxide.[21]

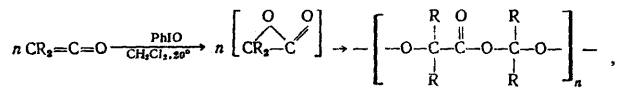
The stability of the iodoso-compounds of all classes is low; they disproportionate on storage:[4,21]

$$2R{-}IO \rightarrow R{-}I + R{-}IO_2 ,$$
$$R = Ar,\ C_nF_{2n-1} .$$

2. Properties

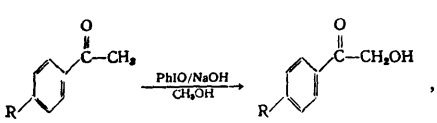
Iodoso-compounds have been used mainly as oxidants. Scant information about the early studies may be found in reviews.[2,4] A number of new reactions involving oxidation by iodosobenzene have been described in a series of communications.[23–25]

Fruitful researches into the oxidation of compounds of a wide variety of classes by iodosobenzene in an alkaline medium were initiated in the 1980's. Ketens give rise to unstable α-lactones, which polymerise at the instant of formation:[26]



R = n-C_4F_9, CF_3, Ph, $PhCH_2$. 32–90%

Acetophenones (I) are oxidised to ω-hydroxyacetophenones (II):[27]

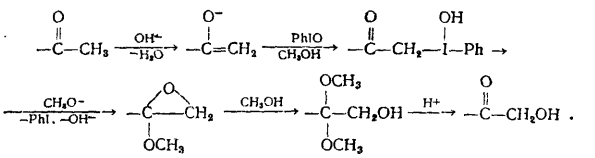


(I) (II), 45–71%

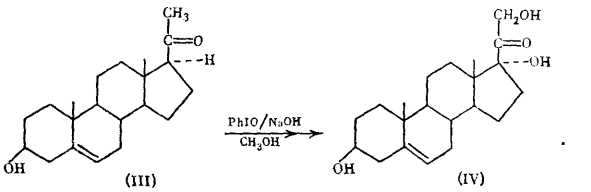
R=H, CH_3, OCH_3, F, Cl, Br, I, NO_2 .

2,6-Diacetylpyridine is oxidised by phenyl iodosoacetate (PIA) in an alkaline medium to 2,6-di(hydroxyacetyl)pyridine in 63% yield.[27]

The acetyl group can be converted to the hydroxy-acetyl group via the following scheme:[28,29]



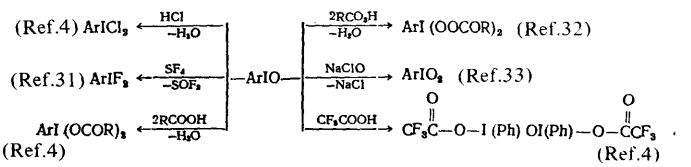
The reaction discovered made it possible to transform the steriod derivative (III) into the derivative (IV) with a high yield:[29,30]



(III) (IV)

Iodosobenzene converts tetracyanoethylene into the corresponding epoxide in 74% yield.[26]

Iodosoarenes can be readily converted into organic compounds of polyvalent iodine belonging to different classes:[4,31–33]

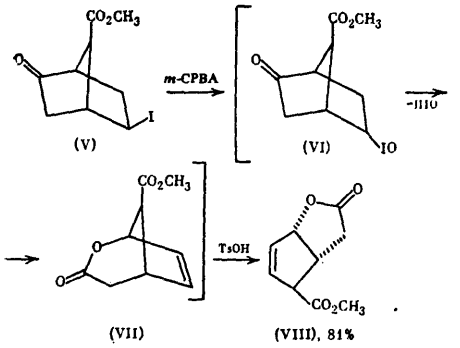


(Ref.4) (Ref.4) (Ref.32) (Ref.31) (Ref.33) (Ref.4)

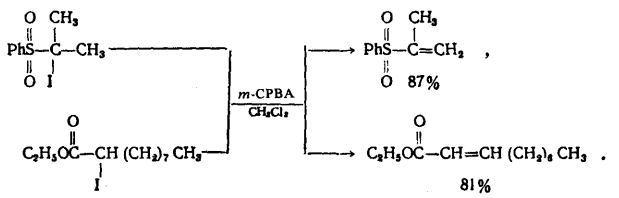
(a) Oxidation Reactions of Alkyl Iodides#, §

Alkyl iodides are resistant to the action of $KMnO_4$, H_2O_2, or O_3 but under the influence of certain oxidants, usually peracids, they are converted into esters or ethers, vicinal diesters, α-iodoesters, alcohols, ketones, or oxirans.[37–40] The mechanisms of these reactions have not so far been ultimately elucidated but the intermediate formation of aliphatic iodoso-derivatives is usually postulated.

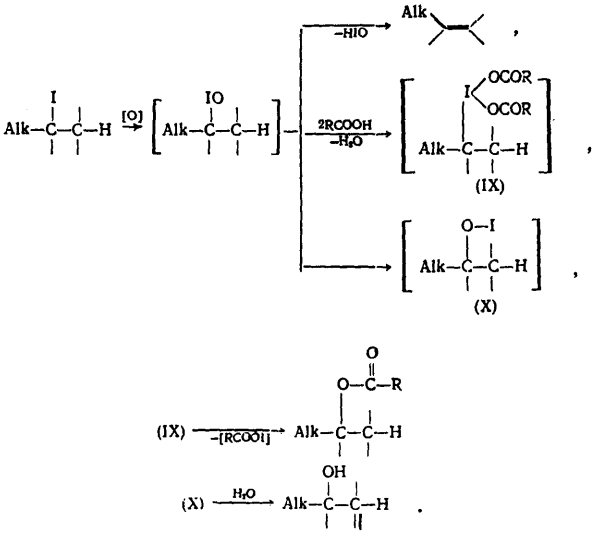
The reaction involving the conversion of the bicyclic iodide (V) under the influence of *m*-chloroperbenzoic acid (m-CPBA) to the lactone (VIII) was described in 1977. The lactone is probably formed via the iodoso-derivative (VI) which is converted into the unsaturated bicyclic lactone (VII) by splitting off HIO:[41]



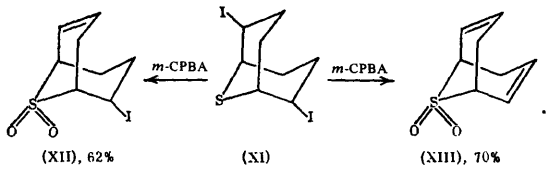
Many details of the reaction of alkyl iodides with peracid were elucidated by Reich and Peake.[42] In a neutral medium, primary alkyl iodides are oxidised by *m*-CPBA to alcohols with a satisfactory yield. Alkyl iodides having electron-accepting groups in the α-position converted into alkenes:



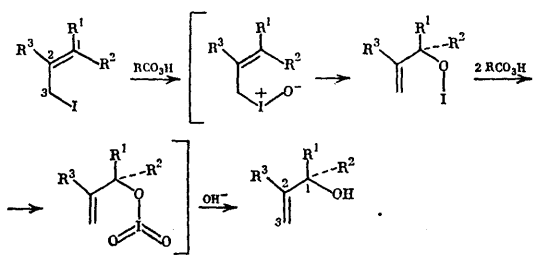
In all cases the initial oxidation products are iodoso-compounds whose subsequent fate depends on the structure of the alkyl iodide. The iodoso-compound can split off hypoiodous acid (*syn*-elimination) or can react with the organic acid to form the iodosocarboxylate (IX), which is not isolated and is converted further into an ester. A rearrangement of the iodoso-compound via a radical or ion pair into the alkyl hypoiodite (X) with subsequent hydrolysis to an alcohol is also possible:



On oxidation with *m*-CPBA, the bicyclic sulphide (XI) gives rise to the unsaturated sulphones (XII) or (XIII) depending on the reaction conditions:[43]



Allyl iodides are oxidised by peracids to allyl alcohol via the intermediate formation of derivatives of tervalent and quinquevalent iodine {the reaction involves a [2,3]sigmatropic rearrangement}:[44]



Alkyl iodides are converted into alkyl fluorosulphates under the influence of peroxydisulphuryl difluoride:[45]

$$AlkI \xrightarrow[CCl_2F_2/-50^\circ]{F-S(=O)_2-O-O-S(=O)_2-F} AlkI(OSO_2F)_2 \xrightarrow[-[FSO_3I]]{-20\div-40^\circ} AlkOSO_2F \quad (52–84\%)$$

Alk=CH_3, CF_3, n-C_3F_7.

The reactions of alkyl iodide with phenyl iodosocarboxylates or phenyl iodosohydroxytosylate lead to esters:[46,47]

$$AlkI \xrightarrow[-PhI,\ -[RCOOI]]{PhI(OCOR)_2\ (PhI(OH)OTs)} AlkOCR\ (AlkOTs) \quad (32–80\%)$$

Esters are also formed when alkyl iodides are oxidised by derivatives of μ-oxobisacyloxy(aryl)iodine.[33,47]

#See Zefirov and co-workers.[34–36]

§ In certain studies such reactions are referred to by the term "oxidative deiodination". It cannot be regarded as apt since the reaction RI → RH is usually associated with the term "deiodination". It is probably better to call these reactions "oxidative substitution of an iodine atom".

When alkyl iodides are oxidised with iodine pentafluoride, aldehydes are produced,[48] oxidation with phenyl iodosochloride affords alkyl chlorides,[1] and oxidation with iodine tris(trifluoroacetate) gives rise to alkyl trifluoroacetates.[45]

Alkenes interact with iodine trichloride to form 1,2-dichloroalkanes, which are probably formed via unstable alkyl iodosochlorides.[50]

The oxidation of alkyl iodides in the presence of salts of acids whose anions are superweak nucleophiles leads to the replacement of iodine by the anion of these acids. The reaction described probably proceeds via a stage involving the formation of carbonium ion intermediates:[51,52]

$$CH_3(CH_2)_nI \xrightarrow[CH_2Cl_2,\ -78 \div +50^\circ]{[\text{oxidant}]/M^+OR^-} CH_3(CH_2)_nOR\ ;\quad 20\text{—}70\%$$

R=CH$_3$, CF$_3$, *p*-CH$_3$C$_6$H$_4$.

It is at present difficult to estimate the synthetic value of reactions involving the oxidative substitution of the iodine atom in alkyl iodides, because many communications are only preliminary and do not give experimental details. However, the value of such reactions is apparently very high; for example, the reaction of methylene iodide with nitronium fluoroborate in the presence of tetrabutylammonium perchlorate results in the formation of methylene bisperchlorate, otherwise difficult to obtain, in nearly quantitative yield.[34]

For the biological oxidation of alkyl halides, including alkyl iodides, see Macdonald et al.[53]

(b) Catalytic Oxidation¶

There exists a large group of oxidation reactions in which iodosobenzene is smoothly involved only in the presence of various metal-containing catalysts.

The ability of iodosobenzene to hydroxylate organic compounds in the presence of cytochrome P-450 has been demonstrated.[55,56] Various metal-containing porphyrins are simple models of the active centre of cytochrome P-450. The ease of oxygen transfer from iodosobenzene to organic substrates in the presence of porphyrins containing iron, chromium, or manganese has been demonstrated.[57–61] It is difficult to predict whether these reactions will find applications in preparative organic chemistry, because studies carried out hitherto have been devoted mainly to the elucidation of the mechanism of the enzyme action. However, many reactions take place extremely stereoselectively; for example *cis*-stilbene is epoxidised in a high yield, while the *trans*-isomer is almost inert:

$$cis\text{-Ph—CH=CH—Ph} \xrightarrow[-PhI]{PhIO/TPPFe(III)Cl} Ph—\underset{\diagdown O \diagup}{CH}—CH—Ph\ ;\quad 82\%$$

TPPFe(III)Cl = chloro(5,10,15,20-tetraphenylprophyrinato)iron.

There is apparently no need to use the fairly complex catalysts mentioned above. The ability of iodosobenzene to oxidise readily alcohols to aldehydes and ketones and disubstituted alkynes to α-dicarbonyl compounds at room temperature in methylenechloride in the presence of $RuCl_2$—$P(Ph)_3$ has been demonstrated.[62–64]

In the presence of iron-containing porphyrins, iodosobenzene oxidises sulphides to sulphoxides.[65,66] Certain sulphoxides can be oxidised by this system to the corresponding sulphones.

¶For a brief review, see Meunier.[54]

III. IODOSOHALIDES

1. Iodosochlorides

(a) Synthesis

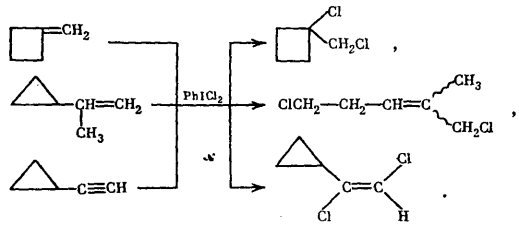
On treatment with chlorine in a solvent, aryl iodides give rise to aryl iodosochlorides.[4] Vinyl iodides are also capable of forming vinyl iodosochlorides. For example, *trans*-diiodoethylene is converted into *trans*-iodovinyl iodosochloride.[67] *trans*-Chlorovinyl iodosochloride can be obtained in a high yield from acetylene.[67–69]

Aliphatic iodosochlorides are as a rule unstable and can be obtained only at low temperatures.[67] The iodosochlorides derived from alkyl iodomethyl sulphones proved to be unexpectedly stable.[70,71]

(b) Chlorination

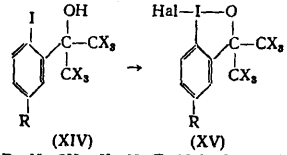
Aryl iodosochlorides are mild chlorinating agents and in solution are able to chlorinate alkenes on thermal or photochemical initiation with formation of vicinal chloride. The reaction mechanism is complex. The reaction can proceed via both radical and ionic mechanisms.[72,73] When alkanes are chlorinated, the tertiary carbon atom is attacked preferentially.[74]

Unsaturated hydrocarbons with cycloalkyl substituents produce high yields of dichlorides.[75,76] It is of interest to note that the trimethylene ring is attacked preferentially in 2-cyclopropylpropene:



Steroid derivatives are also chlorinated by phenyl iodosochloride.[77–79] It has been shown that there is a possibility of the selective halogenation of steroid alcohols with subsequent introduction of a double bond using iodosochlorides based on carboxylic acids having the general formula $Cl_2I.(C_6H_4)_nCOOH$ (n = 0–4), joined to the steroid molecules by ester linkages.[80] The reaction of ethers with phenyl iodosochloride affords the α-chloro-derivatives, while molecular chlorine usually leads to αα′-dichloro-derivatives.[81] Molecular chlorine converts diazoketones into resins, but phenyl iodosochlorine produces geminal dichlorides.[82] The use of phenyl iodosochloride for the chlorination of triphenylphosphine-acylmethylenes has been described.[83,84]

The iodine-containing alcohols (XIV) have been converted into halogeno-iodinanes (XV),[85] which are convenient reagents for benzyl and allyl halogenation:[85]



(XIV) (XV)

R=H, CH$_3$; X=H, F; Hal=Br, Cl, F .

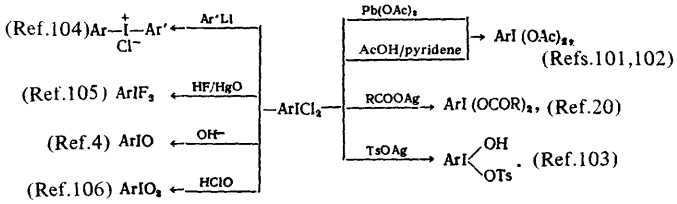
Numerous studies have been made of the influence of polar effects on radical chlorination by aryl iodosochlorides,[86–95] but unfortunately much still remains obscure in this problem.

(c) Oxidation

Phenyl iodosochloride in aqueous pyridine converts sulphides and selenides into sulphoxides and selenoxides.[96,97] Phenyl diphenylmethyl sulphide is cleaved by phenyl iodosochloride to benzenesulphenyl chloride and diphenylmethyl chloride.[98] Secondary steroid alcohols are converted into the corresponding ketones in good yields on treatment with the phenyl iodosochloride–pyridine system.[99] The iodosochloride based on 3-iodopyridine is capable of oxidising selectively secondary alcoholic groups in steroid polyalcohols.[100]

(d) Different Reactions

Like iodoso-compounds, aryl iodosochlorides are widely used in the synthesis of various derivatives of polyvalent iodine:[4, 20,101–106]

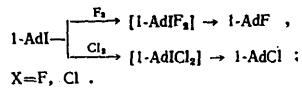


Aryl iodosochlorides are unstable substances which decompose on storage.[4] The main product of the decomposition of phenyl iodosochloride is *p*-chloroiodobenzene.[107]

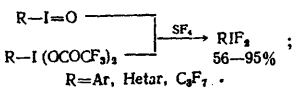
2. Iodosofluorides

(a) Synthesis

They can be obtained from derivatives of univalent or tervalent iodine. Iodosofluorides can be synthesised by fluorinating iodides with elemental fluorine,[108] chlorine trifluoride,[109,110] or xenon difluoride.[111,112] On treatment with molecular fluorine or chlorine, 1-iodoadamantane is converted into 1-fluoro or 1-chloroadamantane via the intermediate formation of iodosohalides, which are not isolated:[113]

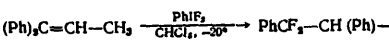


Phenyl iodosofluoride was obtained in a high yield by the electrolysis of silver fluorine in acetonitrile in the presence of iodobenzene.[114] Aryl iodosofluorides can be prepared by condensing iodoso-compounds with 48% hydrofluoric acid[115–117] or by treating iodosochlorides with hydrogen fluoride in the presence of mercury(II) oxide.[105] Iodosofluorides can be synthesised most conveniently by the interaction of iodoso-compounds or iodosotrifluoroacetates with sulphur tetrafluoride:[22]

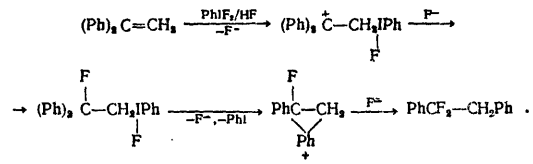


(b) Fluorination

The reaction of 1,1-diphenylethylene with phenyl iodosofluoride affords 1,1-difluoro-1,2-diphenylethane.[105] 3,3-Diphenylprop-2-ene behaves analogously:[118,119]



These reactions probably proceed via a stage involving the formation of a phenonium ion:[120]



Ketones are fluorinated by phenyl iodosofluoride in the α-position.[121] The fluorination of compounds of different classes by methyl iodosofluoride and aryl iodosofluorides has been investigated in a number of studies.[122–125]

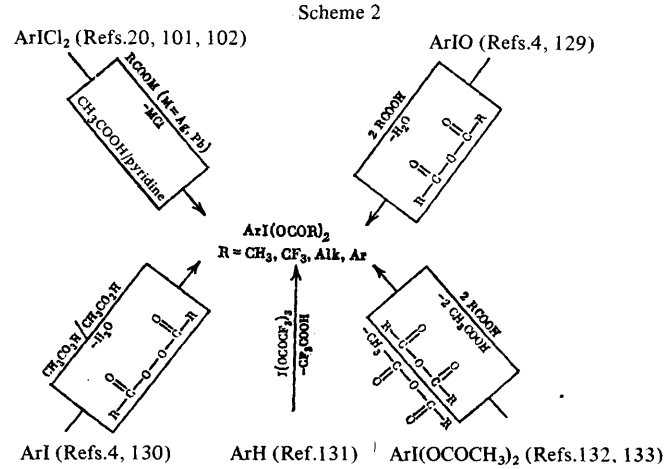
IV. IODOSOCARBOXYLATES

While the nomenclature† of iodonium salts is identical in different countries, the nomenclature of organic compounds of quinquevalent iodine is still in a state of constant development; one would think therefore that the time had come to adopt an unambiguous nomenclature for aryl iodosocarboxylates. For example, more than a dozen different names may be found in the chemical literature of different countries during the last 25 years for the compound $PhI(OCOCH_3)_2$, first synthesised by Willgerodt and called by him phenyl iodoacetate ("Phenyliodacetat").[3] Aryl iodosocarboxylates can probably be named as iodosoesters—derivatives of hydrated iodosoarenes $ArI(OH)_2$, i.e. the compound $PhI.(OCOCF_3)_2$ can be called phenyl iodosotrifluoroacetate, while in the case of partial esters the prefix "hydroxy" is used, for example, the compound PhI(OH)Ts would be called phenyl iodosohydroxytosylate.[127] In the case of mixed iodosoesters, the acid residues forming part of their composition are named alphabetically, i.e. the compound $PhI.(OCOCH_2Br)(OCOCH_2Cl)$ is called phenyliodosobromoacetate-chloroacetate.[128]

1. Synthesis

The scheme presented below illustrates different methods of synthesis of aryl iodosocarboxylates:

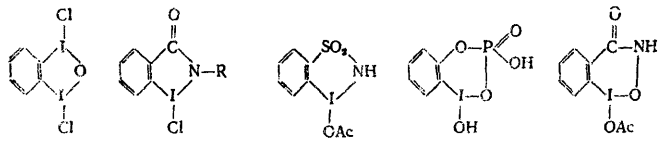
Scheme 2



†For the IUPAC recommendations concerning the nomenclature of organic compounds of polyvalent iodine, see Ref.126.

The reaction of arenes with iodine tris(trifluoroacetate) in trifluoroacetic acid or methylene chloride leads to aryl iodosotrifluoroacetates.[131]

The oxidation of *o*-substituted aryl iodides sometimes leads to the formation of heterocyclic compounds containing tervalent iodine in the ring, for example compounds (XVI)–(XX):[134–139]



(XVI) (XVII) (XVIII) (XIX) (XX)

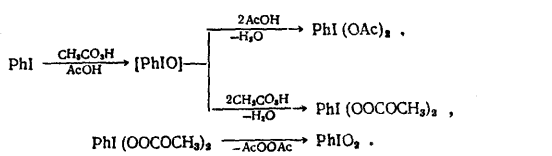
R=CH$_3$, CH$_2$CH$_2$Cl, CH$_2$CO$_2$CH$_3$.

It is of interest to note that phenyl iodoso-*p*-nitrophenylbenzoate is formed on decomposition of *p*-nitrophenylbenzoyl peroxide in iodobenzene.[130] Although this reaction takes place at high temperatures, where aryl iodosocarboxylates usually decompose, it is apparently pssible to select mild conditions for the decomposition of acyl peroxides, whereupon these reactions can become a good preparative method of synthesis of aryl iodosocarboxylates.

Phenyl iodosochloride reacts with lead diacetate or silver salts of carboxylic acids to form phenyl iodosocarboxylates in high yields.[20,101] Aryl iodosochlorides with electron-donating substituents give rise to aryl iodosoacetates on treatment with acetic acid in the presence of pyridine.[102]

The condensation of iodoso-compounds with carboxylic acids also leads to aryl iodosocarboxylates.[4] This reaction is complicated by the instability and poor solubility of iodoso-compounds in the usual organic solvents; it is normally carried out in liquid carboxylic acids, whose excess serves as the solvent (the attempts to condense iodosobenzene with solid carboxylic acids in organic solvents were unsuccessful[140,141]). In these reactions the carboxylic acids can be successfully replaced by their anhydrides.[129,142,143]

The availability of aryl iodosoacetates, their stability on storage, and their ready solubility have made these compounds key reagents in the synthesis of various aryl iodosocarboxylates. Aryl iodosoacetates can be prepared in high yields by oxidising aryl iodides with 30% H_2O_2 in acetic anhydride[144] or with 40% peracetic acid and acetic acid.[145] When iodobenzene is oxidised with the latter reagent, iodoxybenzene may be formed.[146] The mechanism of this process is not entirely clear; iodoxybenzene may be formed on decomposition of the peroxy-compound arising as a result of the condensation of iodosobenzene with peracetic acid:[147]



The exchange reaction of aryl iodosoacetates with substituted benzoic acids can serve as a preparative method of synthesis of the corresponding benzoates.[148,149] Phenyl iodosocarboxylates can be obtained by the exchange reaction between the phenyl iodoso-trifluoroacetate (PITFA) and the sodium salts of carboxylic acid in acetonitrile.[150]

When the exchange reaction between aryl iodosoacetates or aryl iodosotrifluoroacetates and carboxylic acids was carried out in high-boiling solvents at a reduced pressure, it became a universal procedure, which permitted the synthesis of a large series of iodosocarboxylates containing the residues of aliphatic, aromatic, and heterocyclic acids as well as the residues of acylated aminoacids[132] (Table 1):

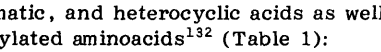


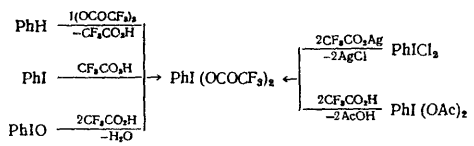
Table 1. Phenyl iodosocarboxylates PhI(OCOR)$_2$.[132]

R	Yield, %	R	Yield, %
Ethyl	72	*o*-Iodophenyl	32
Propyl	81	*o*-Phenylphenyl*	96
Isopropyl	82	*p*-Methoxyphenyl*	83
t-Butyl	82	*p*-Nitrophenyl	96
Diphenylmethyl	85	3,5-Dinitrophenyl	98
Fluoromethyl	91	*o*-Acetoxyphenyl**	62
Chloromethyl	94	*o*-(2-Formylphenyl)phenyl**	58
Trichloromethyl	82	4-Fluorenonyl**	98
2,4-Dichlorophenoxymethyl	92	2-Furyl	60
Phenyl	96	*N*-Benzoylglycyl	92
o-Bromophenyl	66	*N*-Benzoyl-DL-alanyl	96

*The solvent used for the exchange reaction was o-dichlorobenzene.

**Solvent–nitrobenzene.

The methods of synthesis of two phenyl iodosocarboxylates, namely PhI(OCOCF$_3$)$_2$ and PhI(OH)OTs, which have become in recent years multipurpose reagents for organic synthesis, merit special consideration. Phenyl iodosotrifluoroacetate can be prepared from benzene, iodobenzene, phenyl iodosochloride, and phenyl iodosoacetate (PIA):[4,20,131,132,151]



The best of these methods involves the exchange reaction of phenyl iodosoacetate with trifluoroacetic acid. It occurs on simple recrystallisation of PIA from warm (but not boiling) trifluoroacetic acid.[132,151]

Phenyl iodosohydroxytosylate (PIHT) can be prepared by condensing silver tosylate with phenyl iodosochloride or by the exchange reaction of toluene-*p*-sulphonic acid with phenyl iodosoacetate.[103,127] The latter method is more convenient.

2. Oxidation Reactions

All the numerous reactions of aryl iodosocarboxylates with organic compounds can be divided into two large groups. The first group embraces reactions during which aryl iodosocarboxylates are reduced to iodoarenes and various oxidation products not containing iodine are formed from organic substrates. Reactions during which aryl iodosocarboxylates are not reduced and the compounds formed contain a tervalent iodine atom may be assigned to the second group.

Almost all the oxidation reactions in the first group can be subdivided into three subgroups. The first includes reactions of aryl iodosocarboxylates with various acids (OH, NH, and SH- etc. acids). Reactions of aryl iodosocarboxylates with unsaturated compounds, usually leading to acyloxylation

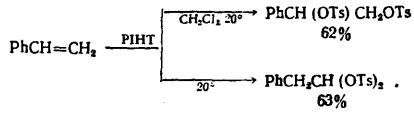
products, belong to the second sub-group. The third sub-group comprises the oxidation reactions of compounds containing heteroatoms (S, P, Se) with formation of the corresponding oxides.

The reactions of the second group are subdivided into two subgroups: the formation of iodonium salts and iodonium ylides.

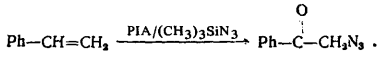
(a) Alkenes

When alkenes react with PIA, PITFA, or PIHT, vicinal diesters are formed.[140,152-154]

On treatment with PIHT, styrene is converted either into 1-phenyl-1,2-di(tosyloxy)ethane or into 2-phenyl-1,1-di(tosyloxy)ethane depending on the reaction conditions:[154]

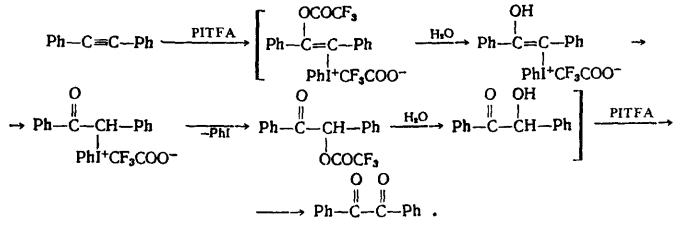


Propene reacts with the PIA/I_2 system to form 2-acetoxy-1-iodopropane in a high yield.[24] The reaction of this system with keten leads to the mixed anhydride of acetic and iodoacetic acids, which can be converted into iodoacetic acid or its anhydride.[155] On treatment with the PIA/$(CH_2)_3SiN_3$ system, styrene is converted into an azide:[156]

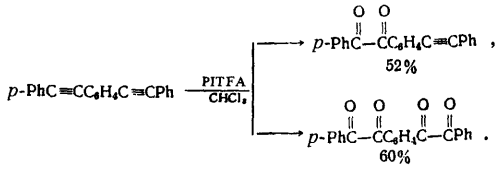


(b) Alkynes

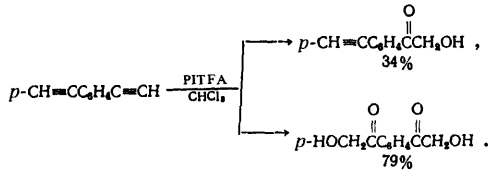
Diarylacetylenes are inert when acted upon by both PIA and lead tetraacetate.[157] However, PITFA oxidises tolanes with electron-donating and not very strong electron-accepting substituents in moist chloroform to the corresponding benzils in good yields.[158] The reaction probably proceeds with the intermediate formation of vinyl- and alkyl-iodonium salts:[158]



We have shown that PITFA oxidises 1,4-di(phenylethynyl)benzene to 4-phenylglyoxaloyltolane or to 1,4-di(phenylglyoxaloyl)benzene:[159]

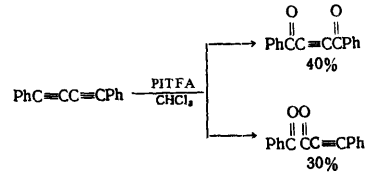


Depending on the reaction conditions, p-diethynylbenzene is converted into 1-ethynyl-4-hydroxyacetylbenzene or into 1,4-di(hydroxyacetyl)benzene:[160]

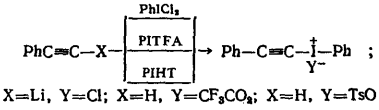


It must be emphasised that at present PITFA is the only reagent capable of oxidising selectively one triple bond in the molecules of polyacetylenic compounds.

Diphenylbutadiyne is oxidised by PITFA to a mixture of dibenzoylacetylene and phenyl(phenylglyoxaloyl)acetylene:[161]



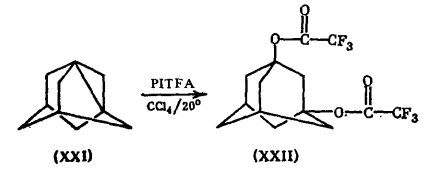
Phenylacetylene reacts with phenyl iodosochloride, PITFA, or PIHT to form acetylenic iodonium salts:[159,162,163]



The stability of such salts increases with decrease of the nucleophilicity of the anion. Disubstituted acetylenes react with the PIA/I_2 system to form *trans*-β-acetoxy-α-iodoalkenes, which readily hydrolyse to α-hydroxyketones.[164]

(c) Cyclopropanes

Various cyclopropylphenyl iodosoacetates were synthesised for the first time in 1979.[165] The three-membered ring in phenylcyclopropane is opened by PITFA with formation of 1-phenyl-1,3-bis(trifluoroacetoxy)propanes.[166] The same reaction takes place also with PIA in a chloroform–trifluoroacetic acid mixture, in which PITFA is formed *in situ*.[167] The strained 1,3-dehydroadamantane (XXI) interacts with PITFA to form the unstrained 1,3-bis-(trifluoroacetoxy)-adamantane (XXII) in a high yield:[168]



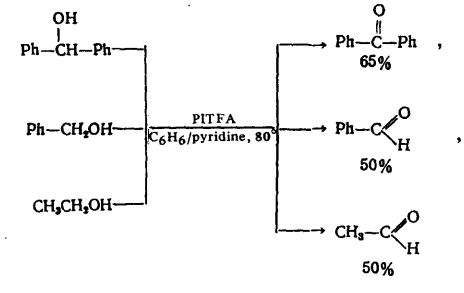
(XXI) (XXII)

(d) Polynuclear Condensed Hydrocarbons

9,10-Dihydroanthracene is dehydrogenated by PITFA or phenyl iodosophthalimidate to anthracene.[151,169] PITFA can oxidise anthracene further to a mixture of 1,2- and 9,10-anthraquinones.[170]

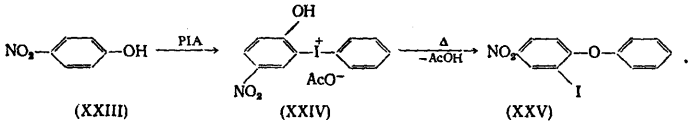
(e) Alcohols, Glycols, Phenols, and Hydroperoxides

Alcohols of different classes react with PIA or PITFA, being oxidised to carbonyl compounds:[4,151]



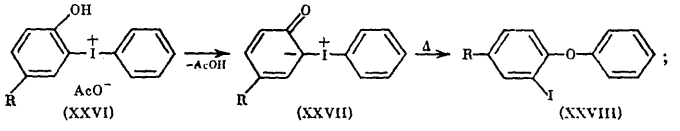
Phenyl iodosoacetate oxidises alcohols in the form of halogenomagnesium alkoxides generated *in situ* from the alcohols and n-propylmagnesium bromide.[171]

The reaction involving the oxidation of phenols by PIA yields a complex mixture of products, in which quinones and o-acetoxyphenols predominate.[172] 4-Nitrophenol (XXIII) is converted into 2-hydroxy-5-nitrodiphenyliodonium acetate (XXIV), which can rearrange on heating via a reaction having an unknown mechanism into 2-iodo-4-nitrophenyl phenyl ether (XXV):[148]



(XXIII) (XXIV) (XXV)

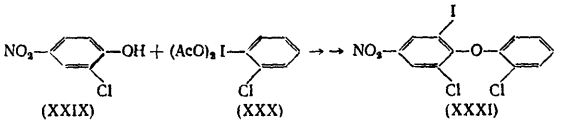
The oxidation of p-ethoxycarbonyl-, p-formyl-, or p-acetylphenols proceeds analogously. The iodonium salts (XXVI), formed initially, split off an acetic acid molecule and are converted into the iodonium ylides (XXVII), which can rearrange to the diphenyl ethers (XXVIII):[173]



(XXVI) (XXVII) (XXVIII)

R = NO_2, $COOC_2H_5$, CHO, $COCH_3$.

2-Chloro-4-nitrophenol (XXIX) is oxidised by 2-chlorophenyl iodosoacetate (XXX), forming 2-chlorophenyl 2-chloro-6-iodo-4-nitrophenyl ether (XXXI):[174]

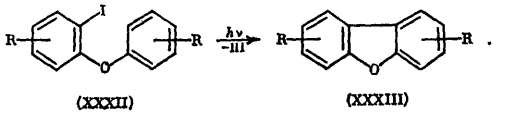


(XXIX) (XXX) (XXXI)

However, 2,6-dichloro-4-nitrophenol is oxidised by PIA to 2,6-dichloro-1,4-benzoquinone.[148]

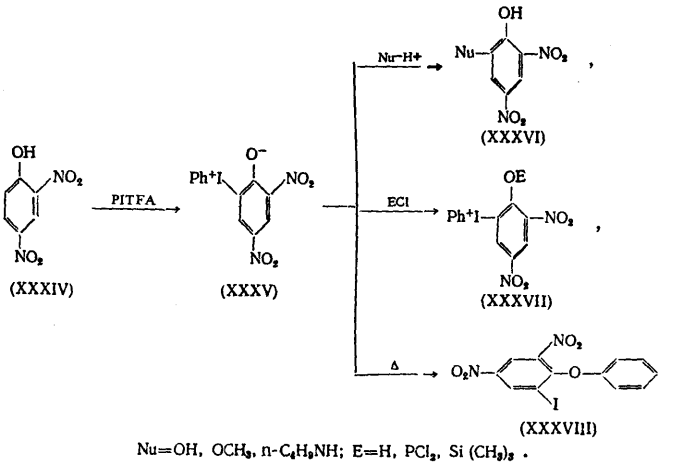
The facts presented permit the conclusion that this interesting reaction is probably general among phenols having an electron-accepting group in the p-position and at least one free o-position.

Photochemical syntheses based on 2-iodo-substituted diphenyl ethers (XXXII) lead to a simple way of preparing substituted dibenzofurans (XXXIII) (see, for example, Kappe et al.[175]):



(XXXII) (XXXIII)

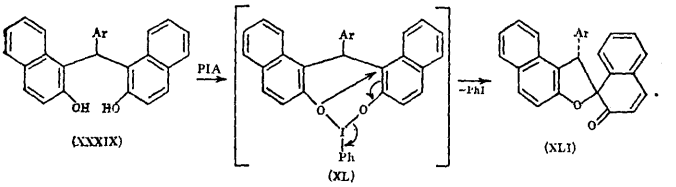
2,4-Dinitrophenol (XXXIV) is oxidised by PITFA to the iodonium salt (XXXV); the latter can react with both nucleophiles and electrophiles, forming the products (XXXVI) and (XXXVII); on heating, compound (XXXV) rearranges to 6-iodo-2,4-dinitrophenyl phenyl ether (XXXVII):[176]



(XXXIV) (XXXV) (XXXVI) (XXXVII) (XXXVIII)

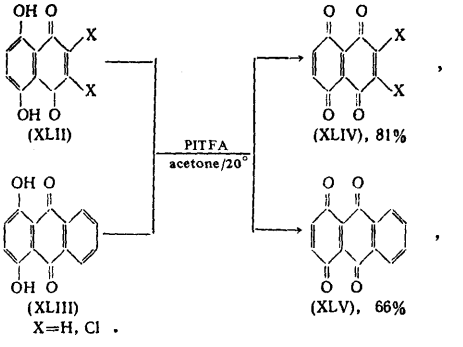
Nu=OH, OCH_3, n-C_4H_9NH; E=H, PCl_2, $Si(CH_3)_3$.

The bisnaphthols (XXXIX) rearrange under the influence of PIA into the spiro-compounds (XLI) via the iodosoethers (XL):[177,178]



(XXXIX) (XL) (XLI)

The reaction of catechol with PIA affords o-benzoquinone in 90% yield.[179] PITFA oxidises 2,3-dichloro-5,6-dicyanohydroquinone to 2,3-dichloro-5,6-dicyanoquinone in 90% yield.[151] PITFA converts the anhydride of hydroquinone-2,3-dicarboxylic acid quantitatively into the anhydride of p-benzoquinone-2,3-dicarboxylic acid.[180] The oxidation of the dihydroxyquinones (XLII) and (XLIII), derived from naphthalene and anthracene, by treatment with PITFA results in the formation of the corresponding diquinones (XLIV) and (XLV):[181]



(XLII) (XLIV), 81%

(XLIII) (XLV), 66%

X=H, Cl .

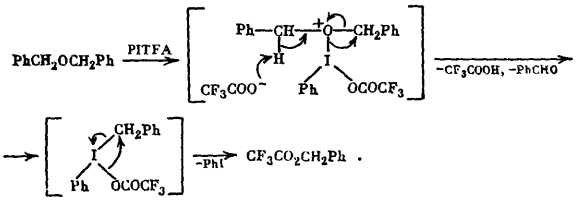
t-Butyl hydroperoxide interacts with PIA at a low temperature to form a new peroxide, which decomposes on raising the temperature:[182]

$$PhI(OAc)_2 \xrightarrow[-2AcOH]{2\ t\text{-}BuOOH} [PhI(OOBu\text{-}t)_2] \rightarrow PhI + O_2 + (t\text{-}BuO)_2 .$$

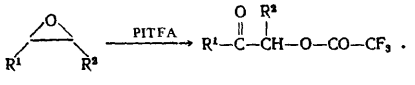
(f) Ethers

On treatment with PITFA, alkyl aryl ethers are converted into iodonium salts.[183] Benzyl ethers are cleaved by PITFA to carbonyl compounds and benzyl or alkyl trifluoroacetate.

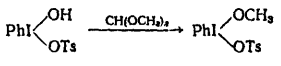
This reaction proceeds via the intermediate formation of an oxonium complex, which is converted, with formation of a carbonyl compound, into a tervalent iodine derivative, which then decomposes to iodobenzene and trifluoroacetate:[184]



Oxirans are converted by PITFA into the trifluoroacetate of α-hydroxyketones:[185]



On reaction with trimethyl orthoformate, PIHT is converted into phenyl iodosomethoxytosylate:[186]

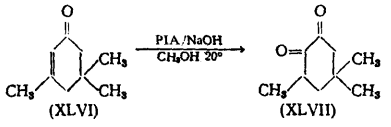


(g) Aldehydes and Ketones

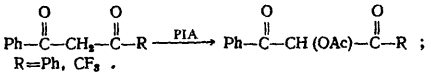
After prolonged contact with PITFA, benzaldehyde is oxidised to benzoic acid. This reaction probably proceeds via the intermediate formation of the mixed anhydride of benzoic and trifluoroacetic acids.[187]

Cyclohexanone reacts with PIA to form 2-hydroxycyclohexanone in 80% yield.[26]

On treatment with PIA, isophorone (XLVI) is converted into 3,5,5-trimethylcyclohexane-1,2-dione (XLVII):[26]



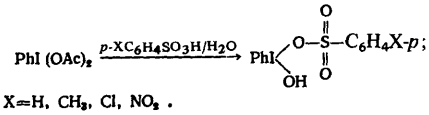
The reaction of acetophenones with PIA in the presence of sulphuric acid leads to products of the acetoxylation of the methyl group.[188] Benzil is cleaved by PITFA to benzoic acid. This reaction probably also takes place via a stage involving the formation of the mixed anhydride of benzoic and trifluoroacetic acids.[160] Dibenzoylmethane and 4,4,4-trifluoro-1-phenylbutane-1,3-dione are acetoxylated on treatment with PIA:[188,189]



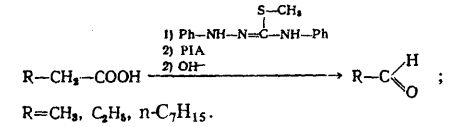
Polycarbonyl compounds are cleaved by PIA to carboxylic acids in aqueous acetic acid.[190]

(h) Carboxylic Acids and Water

Aryl iodosocarboxylates enter into exchange reactions with carboxylic acids.[4] The reactions of PIA with substituted benzenesulphonic acid lead to the corresponding phenyl iodosohydroxybenzenesulphonates:[127]



Carboxylic acids having the methylene group in the α-position react with *S*-methyl-1,4-diphenylisothiosemicarbazide, forming the salts of 5-substituted 3-methylthio-1,4-diphenyl-1,2,4-triazoles. The latter are acetoxylated by PIA at the methylene group and the hydrolysis of the resulting derivative affords aldehydes containing one carbon atom less than the initial acid:[191,192]



The hydrolysis of PIA is the best preparative method of synthesis of iodosobenzene.[19] This reaction proceeds via hydrated iodosobenzene, which loses a water molecule. Under the usual conditions, the reaction requires alkaline catalysts but at elevated temperatures it can take place even under the influence of the traces of moisture present in the solvent (see, for example, Hey et al.[193]).

(i) Primary Aromatic Amines

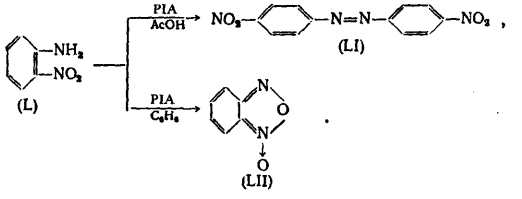
These are oxidised by aryl iodosocarboxylates to azo-compounds under mild conditions with yields ranging from low to excellent. The reaction takes place via a free-radical mechanism.[194–196]

The amino-derivatives (XLVIII) cyclise under the influence of PIA to diazepines (XLIX):[197,199]



The remarkable reaction involving the oxidation of 4-iodoaniline to 4,4′-diiodoazobenzene by chlorine or peracetic acid can be explained by the intermediate formation of iodosochlorides and iodosoacetates.[199,200]

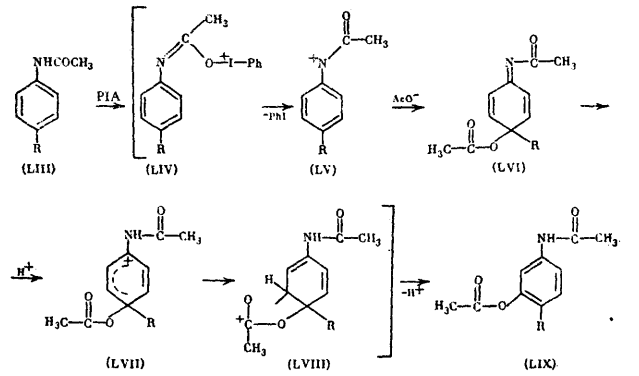
o-Nitroaniline (L) can be oxidised both to 4,4′-dinitroazobenzene (LI) and to benzofuroxan (LII):[196]



2-Amino-3-nitrobiphenylene is converted into the corresponding furoxan in 70% yield.[201] The oxidative cyclisation reaction is common to anilines having in the o-position a substituent capable of forming a heterocyclic ring.[202]

The reactions of the acetanilides (LIII), having electron-donating groups in the 4-position, with PIA proceed in accordance with the heterocyclic mechanism via the iodonium salt (LIV), the nitrenium cation (LV), and the dienoneimine (LVI).

The protonated form of the latter (LVII) rearranges intramolecularly via compound (LVIII) to the 3-acetoxy-derivative (LIX):[203]



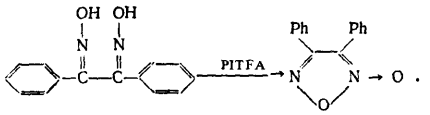
(LIII) (LIV) (LV) (LVI) (LVII) (LVIII) (LIX)

(j) Carboxylic Acid Amides

On reaction with aryl iodosocarboxylates, they are decarbonylated.[204-206] PITFA is a convenient reagent for the stepwise degradation of peptides attached to an insoluble polymeric support.[207]

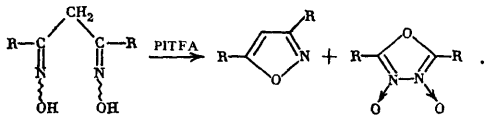
(k) Oximes

α-Dioximes react with PITFA to form mixtures of aldazine di-*N*-oxides and nitrile oxides. The benzil dioxime (LX) is converted into the corresponding furoxan (LXI):[151]



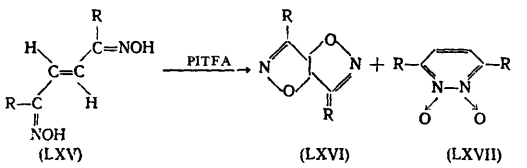
(LX) (LXI), 91%

The β-dioximes (LVII) give rise to mixtures of isoxazoles (LXIII) and 4-oxa-4*H*-pyrazole di-*N*-oxides (LXIV):[208,209]



(LXII) (LXIII) (LXIV)

trans-2-Unsaturated 1,4-dioximes (LXV) react with PITFA to form a mixture of 3*a*,6*a*-dihydroisoxazolo[5,4-*d*]isoxazoles (LXVI) and pyridazine 1,2-dioxides (LXVII):[210]



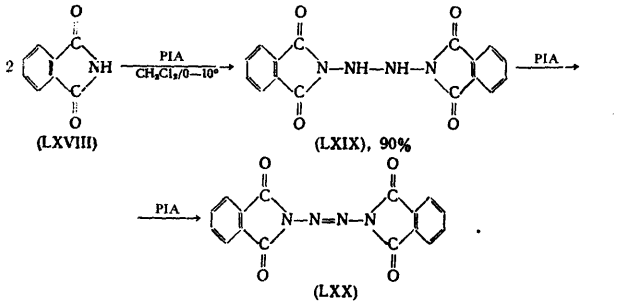
(LXV) (LXVI) (LXVII)

(l) Various Nitrogen-containing Compounds

Hydrazobenzene is dehydrogenated quantitatively by PIA to azobenzene.[194] PITFA converts diethyl hydrazodicarboxylate into diethyl azodicarboxylate;[151] PIA is ineffective in this reaction.

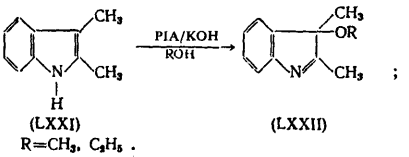
Schiff bases are oxidised by PIA with formation of aldehydes and azo-compounds.[211] The interaction of *NN*-dibenzylhydroxylamines with PIA leads to nitrones.[212]

Phthalimide (LXVIII) is oxidised by PIA to the tetrazane (LXIX), which can be converted further into the tetrazene (LXX):[213]



(LXVIII) (LXIX), 90% (LXX)

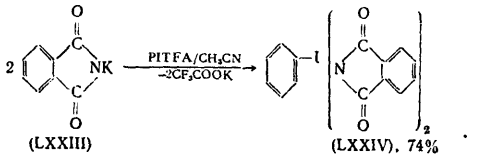
4-Amino-3,5-diphenyl-1,2,4-triazole reacts with PIA to form benzonitrile; in the presence of alkenes, this reaction can lead to aziridines.[214] The reactions of PIA with aryldiazomethanes or 1-aryl-1-diazoethanes affords complex mixtures of products, the main components of which are the trifluoroacetates $ArCH_2OCOCF_3$ or $ArCH(CH_3)OCOCF_3$.[215] On treatment with PIA in the presence of alkali in alcohols, 2,3-dimethylindole (LXXI) gives rise to 3-alkoxyindolenine (LXXII):[216]



(LXXI) (LXXII)

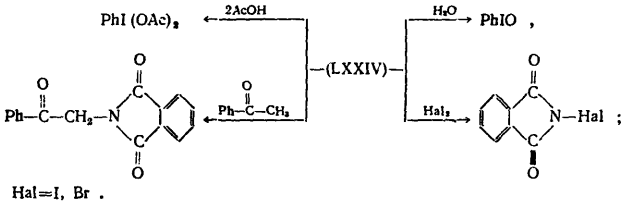
R=CH_3, C_3H_5 .

Phenyl iodosophthalimidate (LXIV) is obtained by the reaction of potassium phthalimide (LXXIII) with PITFA:[169]



(LXXIII) (LXXIV), 74%

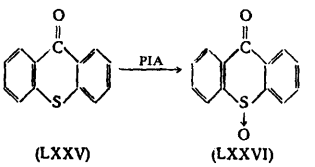
Compound (LXXIV) enters into a series of reactions:[169]



Hal=I, Br .

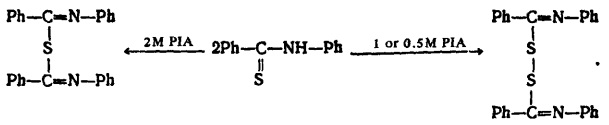
(m) Sulphur-containing Compounds

Thiophenols are oxidised to disulphides on treatment with both PIA [217] and PITFA.[151] The oxidation of sulphides by PIA leads to sulphoxides.[218,219] When the thiaxanthone (LXXV) is treated with PIA, it is converted into the corresponding sulphoxide (LXXVI) in a high yield:[220]



(LXXV) (LXXVI)

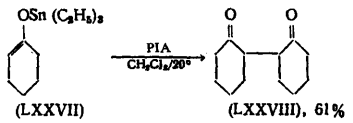
It is of interest to note that phenyl trityl and benzyl trityl sulphides are not oxidised by PIA to the corresponding sulphoxides but are cleaved with formation of diphenylmethanol and probably compounds containing bivalent sulphur.[221] The oxidative elimination of sulphur from various sulphur-containing compounds is possible. On treatment with PIA, thiobenzanilide is converted into benzanilide in aqueous ether.[222] Depending on the reaction conditions, in absolute ether thiobenzanilide is converted into di(α-phenyliminobenzyl) sulphide or into di(α-phenyliminobenzyl) disulphide:[222]



(n) Compounds Containing Phosphorus, Selenium, Boron, and Tin

The reaction of triphenylphosphine with PITFA leads to triphenylphosphine oxide.[8] Selenazines react with PIA to form the corresponding selenazine oxides.[223]

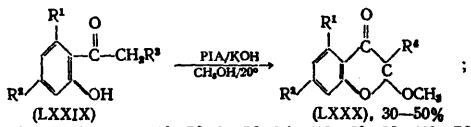
Phenyl iodosoacetate is capable of oxidising boron compounds.[224,225] The triethylstannyl enolate of cyclohexanone (LXXVII) is converted on treatment with PIA into 2,2'-dioxo-1,1'-bicyclohexyl (LXXVIII):[226]



(LXXVII) (LXXVIII), 61%

(o) Polyfunctional Compounds

The reaction of benzoin with PITFA results in the formation of benzil in a high yield.[158] The interaction of *o*-hydroxyacetophenones (LXXIX) with PIA in the presence of KOH affords coumaran-3-ones (LXXX):[227]

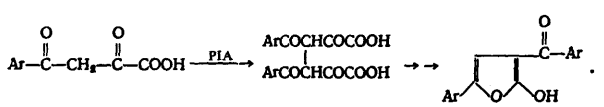


(LXXIX) (LXXX), 30–50%

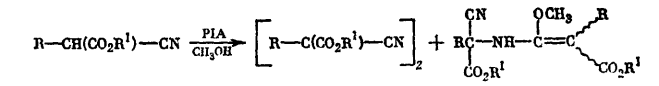
$R^1=R^2=R^3=H$, $R^4=OCH_3$; $R^1=R^2=H$, $R^3=R^4=CH_3$; $R^1=R^3=CH_3$, $R^2=H$, $R^4=OCH_3$; $R^1=R^3=H$, $R^2=R^4=PhCH_2$.

The oxidation of 3-cyanopyrrolidine-2,5-diones with PIA leads to the formation of ring opening products.[228] *NN*-Dialkyl-2-aminoalcohols are cleaved by PIA to aldehydes and iminium salts; the latter hydrolyse to amines and formaldehyde.[229] On treatment with PIA or iodosobenzene, α-ketoacids are decarbonylated.[26,140,230]

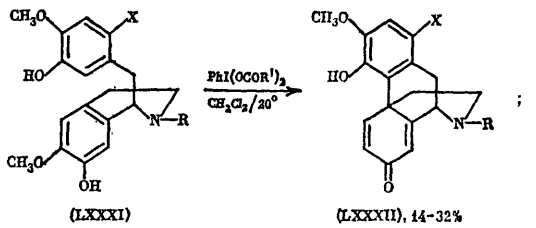
α-Hydroxyacid esters are oxidised by PIA to α-ketoacid esters.[231] 4-Aryl-2,4-dioxobutanoic acids are cyclised by PIA to 4-aroyl-2-aryl-5-hydroxyfurans:[232]



When α-cyanocarboxylates are treated with PIA, they dimerise:[233]



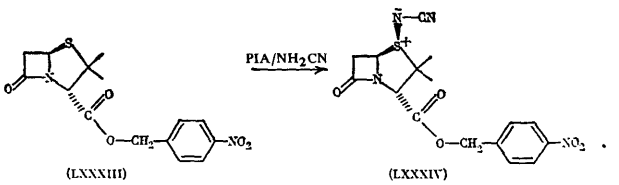
Reticuline (LXXXI) is cyclised by phenyl iodosocarboxylates to salutaridine (LXXXII):[133]



(LXXXI) (LXXXII), 14–32%

X=H, Br, Cl; R=CH_3, , $CO_2C_2H_5$; R'=CH_3, CCl_3, CF_3 .

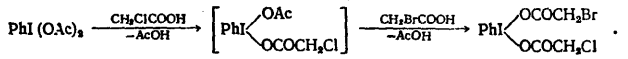
The PIA/cyanamide system converts the penicilloic acid derivative (LXXXIII) into the derivative (LXXXIV):[234]



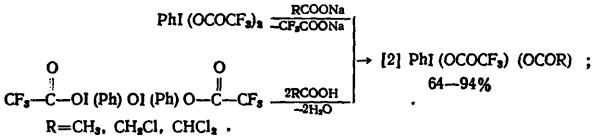
(LXXXIII) (LXXXIV)

(p) Mixed Iodosocarboxylates

For a long time, the sole representative of these compounds was phenyl iodosobromoacetate-chloroacetate synthesised from PIA:[128]



Iodosocarboxylates contain the residues of various acids, one of which is trifluoroacetic acid, and can be conveniently obtained from PITFA [150] or from μ-oxobis(trifluoroacetoxy)-(phenyl)iodine:[33]



R=CH_3, CH_2Cl, $CHCl_2$.

Cyclohexene reacts with phenyl iodosoacetate-trifluoroacetate to form 1-acetoxy-2-trifluoroacetoxycyclohexane, which readily hydrolyses to 2-acetoxycyclohexanol.[150]

(r) Catalytic Oxidation

Like iodosobenzene, aryl iodosocarboxylates are able to hydroxylate organic compounds in the presence of cytochrome P-450.[235] Tolan is oxidised by the PIA/$RuCl_2$–$P(Ph)_3$ system to benzil [63] and 1-octanol is oxidised to 1-octanal.[62] PIA in aqueous acetic acid containing $RuCl_3$ cleaves fumaric, maleic, arylic, and cinnamic acid as well as styrene at the carbon–carbon double bonds.[236] It has recently been possible to isolate the complex formed in the reaction of PIA with the manganese-containing porphyrin: PhI(OAc)–O–Mn(IV)–O–I(OAc)Ph. This complex hydroxylates organic compounds.[237]

3. Direct Halogenation of Aromatic and Heteroaromatic Compounds

The possibility, in principle, of iodinating *m*-xylene in warm acetic acid by the I_2/PIA or I_2/PhIO system was demonstrated in 1963.[238] Azobenzene is iodinated by the I_2/PIA system in boiling acetic acid, forming 4-iodoazobenzene in a low yield.[239] These iodinating systems have not found extensive application in synthetic organic chemistry. The observation of a fairly unexpected iodination of iodobenzene to *p*-diiodobenzene in a high yield by the I_2/PITFA system in carbon tetrachloride at room temperature[160] led the authors[170,240,241] to investigate the preparative possibilities of this reaction.

The iodination takes place readily at room temperature when equimolar amounts of PITFA and iodine are mixed with the organic substrate in methylene chloride, chloroform, carbon tetrachloride, or 1,2-dichloroethane:

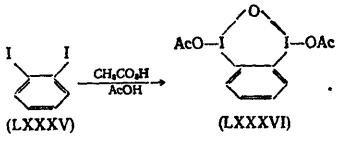
$$R{-}H \xrightarrow[-PhI,\ -CF_3COOH]{I_2/PITFA} R{-}I\ ;$$
R=Ar, Hetar .

This system iodinates compounds which are more reactive in electrophilic substitution reactions than iodobenzene. There is no need to employ PITFA which is unstable on storage—it can be generated in situ from PIA and trifluoroacetic acid.[170]

This method is effective for the direct iodination of arylcyclopropanes.[242] The Br_2/PITFA system is convenient for bromination of arenes,[243,244] while the $AlCl_3$/PITFA system is convenient for chlorination.[244] Because of its experimental simplicity, the possibility of carrying out the halogenation at room temperature, and the ease with which the target products can be isolated, the above halogenation method can find extensive application in fine organic synthesis. Certain data on these processes are presented in Table 2.

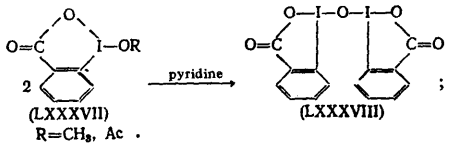
V. DERIVATIVES OF μ-OXOBISACYLOXY(ARYL)IODINE

Although these compounds have been known for a long time, it is noteworthy that until recently there was no convenient method of their synthesis. The oxidation of o-diiodobenzene (LXXXV) with peracetic acid yields the μ-oxo-compound (LXXXVI):[134]



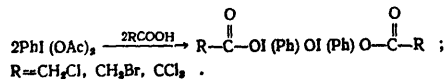
(LXXXV) (LXXXVI)

On treatment with pyridine, derivatives of *o*-iodosobenzoic acid (LXXXVII) give rise to the μ-oxo-compound (LXXXVIII):[141]



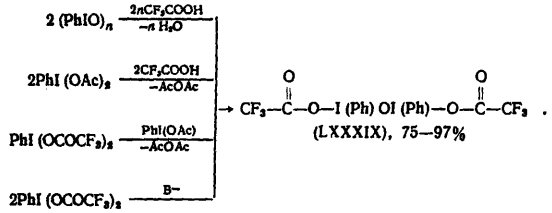
(LXXXVII) (LXXXVIII)
R=CH_3, Ac .

μ-Oxo-compounds can be obtained from PIA:[245]



R=CH_2Cl, CH_2Br, CCl_3 .

A series of effective approaches to the synthesis of μ-oxo-bis(trifluoroacetoxy)(phenyl)iodine (LXXXIX) have been proposed:[33]



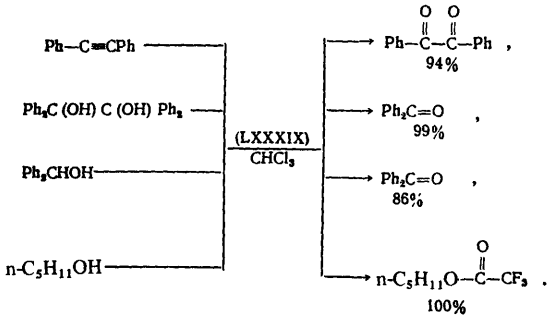
(LXXXIX), 75—97%

Table 2. The synthesis of halogeno-derivatives by halogenation in the presence of PITFA.

Organic substrate	Halogeno-derivative	Yield, %	Refs.
Benzene*	iodobenzene	72	[170]
o-Xylene	4,5-diiodo-*o*-xylene	55	[240]
m-Xylene	4,6-diiodo-*m* xylene	77	[240]
p-Xylene	2,5-diiodo-*p*-xylene	65	[240]
Mesitylene	triiodomesitylene	84	[240]
Durene	diiododurene	52	[240]
Phenylcyclopropane	4-iodophenylcyclopropane	42	[242]
Biphenyl	4,4-diiodobiphenyl	87	[240]
p-Terphenyl	4,4′-diiodo-*p*-terphenyl	93	[170]
Diphenylmethane	4,4′-diiododiphenylmethane	50	[170]
Chlorobenzene*	4-chloroiodobenzene	61	[240]
Bromobenzene*	4-bromoiodobenzene	63	[240]
Iodobenzene*	1,4-diiodobenzene	73	[240]
Diphenyl ether	di(4-iodophenyl) ether	79	[240]
Fluorenone	2,7-diiodofluorenone	51	[240]
Biphenyl-4-carboxylic acid	4-iodobiphenyl-4′-carboxylic acid	81	[170]
Fluorene-9-carboxylic acid	2,7-diiodofluorene-9-carboxylic acid	70	[240]
Methyl fluorene-9-carboxylate	methyl 2,7-diiodofluorene-9-carboxylate	52	[240]
Diphenylene oxide	2,7-diiododiphenylene oxide	59	[170]
o-Carbaborane	9-iodo-*o*-carbaborane	72	[241]
o-Carbaborane	9,12-diiodo-*o*-carbaborane	74	[241]
m-Carbaborane	9-iodo-*m*-carbaborane	64	[241]
Benzene*	bromobenzene	99	[243]
Mesitylene	tribromomesitylene	82	[243]
Biphenyl	4,4′-dibromobiphenyl	96	[243]
Diphenyl ether	di(40bromophenyl) ether	80	[243]
Fluorenone	2,7-dibromofluorenone	73	[244]
4-Methoxybenzoic acid	3-bromo-4-methoxybenzoic acid	81	[244]
Benzene*	chlorobenzene	80	[244]
Mesitylene	trichloromesitylene	63	[244]
Durene	dichlorodurene	38	[244]
Fluorenone	2,7-dichlorofluorenone	93	[244]

*The reaction was carried out in an excess of the aromatic substrate.

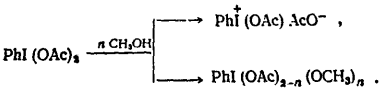
Certain data on the oxidative properties of the compounds obtained are illustrated by the equations presented below:[33]



On treatment with like carboxylic acids, the μ-oxo-compounds are converted into phenyl iodosocarboxylates, while unlike carboxylic acids convert them into mixed iodoso-esters.[245] Treatment of alkenes with the μ-oxo-compounds results in the formation of vicinal diesters.[246]

VI. SPECTROSCOPIC DATA

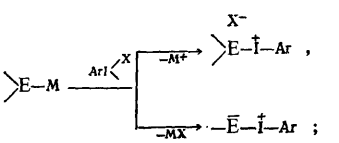
X-Ray diffraction data have been obtained for phenyl iodosochloride,[247] PIA,[248] phenyl iodosodichloroacetate,[249] μ-oxobis(trifluoroacetoxy)(aryl)iodine,[33] and 1-hydroxy-3-oxo-3*H*-benzoiodoxole (the cyclic form of *o*-iodosobenzoic acid).[250] ^1H, ^{13}C, and ^{19}F NMR data have been published for various organic compounds of polyvalent iodine;[31,33,136,251,252] the ^{19}F NMR spectra of perfluoroalkyliodoso-compounds have been discussed.[21,253] The observed splitting of the PIA signal in the ^1H NMR spectrum on reducing the temperature in solution in methanol has been interpreted as evidence for the existence of the ionic and covalent forms of PIA at a low temperature.[254] However, it has been shown[233] that PIA interacts with methanol even at very low temperatures and thus the problem has remained open:



The IR spectra of various polyvalent iodine compounds have been discussed in a series of studies[141,255-257] and the IR and Raman spectra have been described.[15] For data on the dipole moments of aryl iodosocarboxylates, see Exner and Plesnicar.[258] The results of conductimetric studies of solutions of phenyl iodosochloride have been published by Zappi and Cortelezzi[259] and those for PIA solutions can be found in the paper of Johnson and co-workers.[260,261] Erlich and Kaplan[262]# published the Mössbauer spectra for different polyvalent iodine compounds.

VII. IODONIUM ION AND IODONIUM YLIDE FORMATION REACTIONS

So many different methods of synthesis of iodonium salts and iodonium ylides have now been developed that they cannot be represented simply by any one scheme. However, most of them can be described by the equation given below:

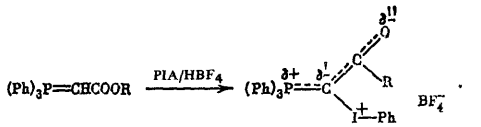


M=Li, Na; E = C, N.

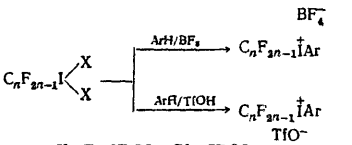
In principle, any polyvalent iodine compounds can be used in iodonium ion formation reactions, but aryl iodosoacetates or iodoso-compounds are most frequently employed.[17] They can be generated *in situ* by oxidising aryl iodides.[263,264]

#According to these data,[262] the chlorine atoms in the molecule of phenyl iodosochloride are entirely equivalent, which fails to provide any kind of justification for the use of the term "aryliodonium chlorides" for aryl iodosochlorides, which can be encountered in some communications.

When the phosphonium ylide is treated with PIA in the presence of HBF_4, a double iodonium salt is obtained[265] (see also Moriarty et al.[266]):

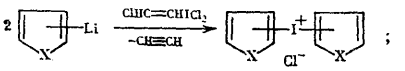


Derivatives of perfluoroiodosoalkanes were found to be extremely useful reagents for the synthesis of iodonium salts:[267-272]



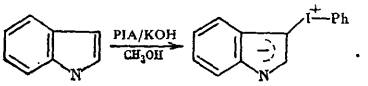
X=F, CF_3CO_2; Tf=CF_3SO_2.

A unique iodonium ion forming agent is PIHT,[163,273-276] which can condense with trimethylsilyl derivatives of furan under neutral conditions to form furylphenyliodonium salts.[274] *trans*-Chlorovinyl iodosochloride is a convenient reagent for the synthesis of heterocyclic iodonium salts:[277-279]



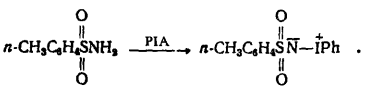
X=S, O, Cl

The reaction of PIA with indole (XC) leads to the formation of an ylide (XCI) with a carbon–iodine bond:[280]

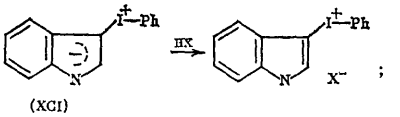


(XC) (XCI)

The interaction of PIA with toluene-*p*-sulphonamide affords an ylide with a nitrogen–iodine bond:[281]



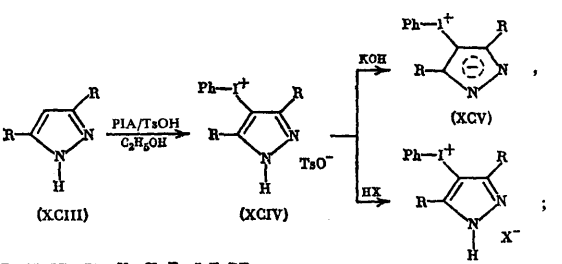
Iodonium salts are most closely related to iodonium ylides and they can sometimes be interconverted. The iodonium ylide (XCI) can be converted into the iodonium salts (XCII):[280]



(XCI)

X = TsO, BF_4, ClO_4.

The iodonium salts (XCIV), obtained from pyrazoles (XCIII), give rise to the iodonium ylides (XCV) or the new iodonium salts (XCVI):[282]



(XCIII) (XCIV) (XCV) (XCVI)

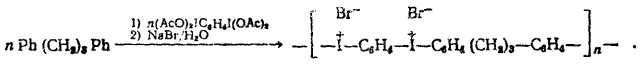
R=H, CH_3, Ph; X= Cl, Br, I, F, BF_4.

VIII. POLYMERS WITH TERVALENT IODINE

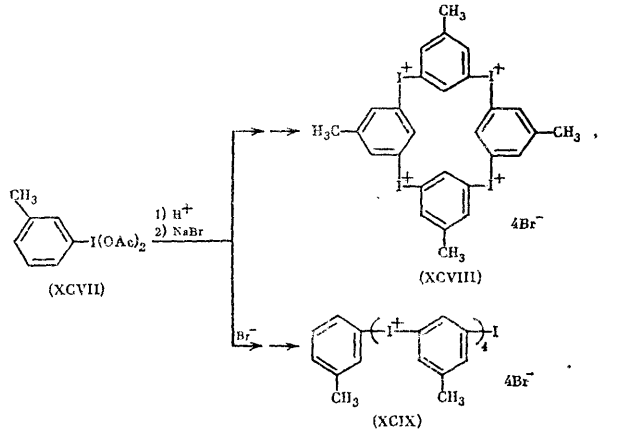
All these polymers can be arbitrarily divided into two groups. The first includes those in the molecules of which the tervalent iodine atom is used to link individual monomer units, while the second group comprises polymers whose monomer units are linked via other atoms and the polyvalent iodine atom enters into the composition of the macromolecule as a functional group.

Condensation of iodosobenzene with succinic anhydride, of PIA with adipic acid, and of phenyl iodosochloride with the silver salt of sebacic acid made it possible to obtain polymers in which the monomer units are linked by a tervalent iodine atom. They are solid brittle substances, insoluble in all the usual organic solvents under the normal conditions, but soluble on heating in some solvents, the dissolution being accompanied by degradation.[283] Unfortunately no data could be obtained about the structure of such polymers.

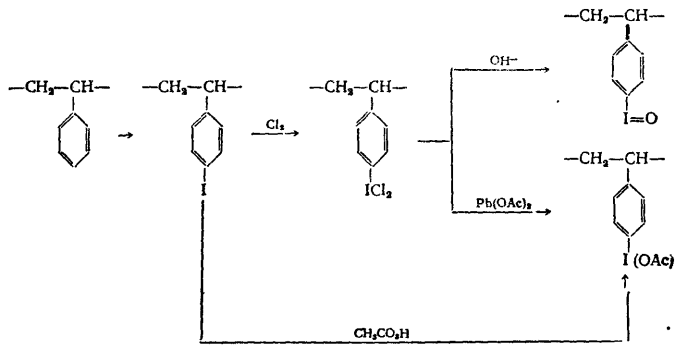
Polymers in which the monomer units are joined together with $-\overset{+}{I}-$groups have been synthesised:[284]



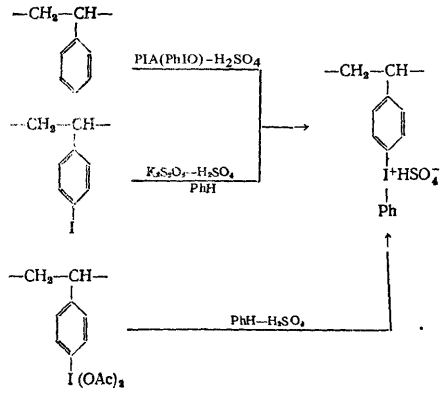
m-Tolyl iodosoacetate (XCVII) forms cyclic or linear tetrameric iodonium ions (XCVIII) and (XCIX) in sulphuric acid:[284]



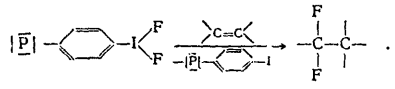
A series of polymers with polyvalent iodine, prepared on the basis of both linear and cross-linked polymers, are known.[285-296] The linear polystyrene can be iodinated in the presence of the oxidants $P_2O_5-H_2SO_4$ and $HIO_3-H_2SO_4$ on heating in nitrobenzene[288,289] in the presence of PITFA at room temperature in chloroform.[291] Poly(*p*-iodostyrene) can be converted into a polymer with polyvalent iodine by the same procedures as iodobenzene:



Polymeric iodonium salts based on linear polystyrene can be obtained with the aid of the reactions given below:[289]

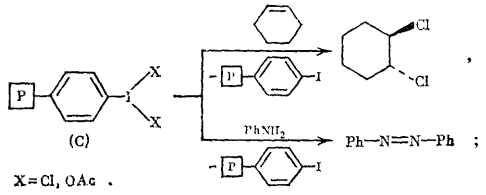


The cross-linked iodinated divyinylbenzene–styrene copolymer produces, on treatment with xenon difluoride, a polymeric reagent with iodosofluoride groups, which fluorinates olefins at room temperature with rearrangement:[292]

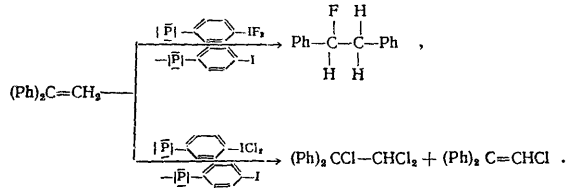


The spent polymer can be separated from the reaction product by simple filtration and can be reused after regeneration.[292]

The iodosochloride (C), obtained from the iodinated cross-linked divinylbenzene–styrene copolymer, reacts with cyclohexene to form *trans*-1,2-dichlorocyclohexane. The polymeric iodosoacetate (C) oxidises aniline to *trans*-azobenzene:[293]



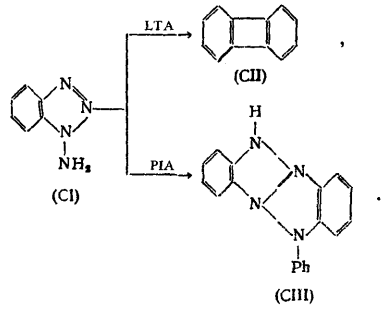
The reaction of 1,1-diphenylethylene with polymeric reagents based on cross-linked iodopolystyrene leads to various halogeno-derivatives:[294]



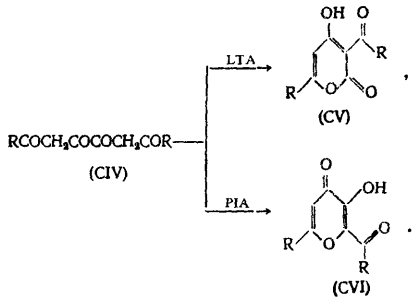
IX. CONCLUSION

Many chemists are under the impression that aryl iodosocarboxylates as oxidants are entirely similar to the popular reagent lead tetraacetate (LTA) (see, for example, Varvoglis[8]). However, in the 1980's a series of oxidation reactions

were discovered, which proceed in a fundamentally different way, depending on whether the oxidant is LTA or PIA. For example, the oxidation of 1-aminobenzotriazole (CI) with LTA leads to the biphenylene (CII) in a high yield,[297] while in the oxidation of compound (CI) by PIA biphenylene is not formed at all and the main product is compound (CIII):[298]



By oxidising the tetraketone (CIV) with LTA or PIA, it is possible to obtain two isomeric pyrones (CV) and (CVI):[299]

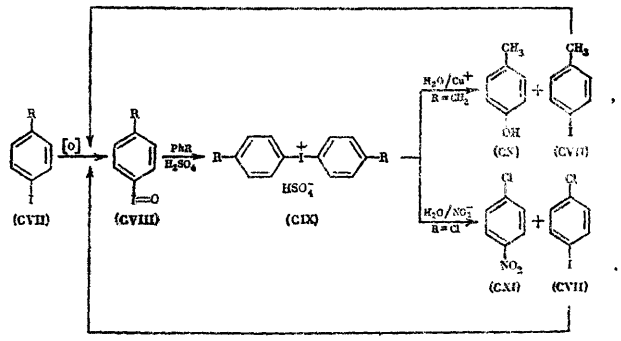


Bearing in mind the definite similarity between LTA and PIA in oxidation reactions, one should note one fundamental difference between these reagents. Their reduction products are lead diacetate in the former case and iodobenzene in the latter and to this day it is definitely easier to separate organic oxidation products from lead diacetate than from iodobenzene. It is noteworthy that PIA, in particular, and phenyl iodosocarboxylates in general can enter into the composition of polymers which are both soluble (for example, iodinated polystyrene) and insoluble (for example, the iodinated divinylbenzene–styrene copolymer). At the present time lead-containing polymers are not used in organic synthesis. These facts suggest that in the future the chemistry of polymeric iodosocarboxylate oxidants will develop. The products of the reduction of such reagents will be polymeric iodoarenes and they can be separated without special difficulty from reaction mixtures by simple filtration.

It is noteworthy that, as a chlorinating agent effecting the addition of chlorine to alkenes via an ionic mechanism, the polymeric iodosochloride resembles molecular chlorine rather than phenyl iodosochloride.[294]

Most attention should be devoted to multipurpose reagents for organic synthesis such as PITFA and PIHT.

There has been a remarkable study which demonstrated the possibility of obtaining *p*-cresol (CX) and *p*-chloronitrobenzene (CXI) by the iodonium ion formation reaction using iodo-derivatives of toluene or chlorobenzene (CVII), which proceeds via the corresponding iodo-derivatives (CVIII) and iodonium salts (CIX):[300]



Taking into account all the foregoing factors, one may conclude that, together with iodonium salts, the most important representative of organic compounds of tervalent iodine are aryl iodosocarboxylates and that new major discoveries are to be expected in the first place in these two fields.

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