

[HYDROXY(TOSYLOXY)IODO] BENZENE : A USEFUL HYPERVALENT
 IODINE REAGENT FOR THE SYNTHESIS OF HETEROCYCLIC
 COMPOUNDS

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Abstract--[Hydroxy(tosyloxy)iodo]benzene, a hypervalent iodine reagent finds extensive use in the synthesis of a wide variety of heterocycles. In this review an effort has been made to present the prolific development in recent years in this area.

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References

1. INTRODUCTION

A surge of interest in the utility of organo-hypervalent iodine reagents in organic synthesis has been observed in recent years,¹⁻⁸ despite the fact that the first hypervalent iodine compound was reported in 1886 by Willgerodt.⁹ As a result, several excellent reviews dealing with the synthetic importance of hypervalent iodine reagents have recently appeared.¹⁻⁸ A particularly noteworthy relevance to the present article is one by Moriarty and Koser⁷ (1990) on the use of [hydroxy(tosyloxy)iodo]-benzene [HTIB, sometimes referred to as Koser's reagent e.g. Aldrich catalogue, 1990-1991].

One of the most striking aspect of HTIB, developed recently is its great synthetic potentiality in the synthesis of heterocyclic compounds. In

view of the fact that this development has opened a new synthetic area of immense value and now a wide variety of heterocyclic compounds can be available by alternative iodine(III) mediated simpler approaches, it is worthwhile to review this feature of the hypervalent iodine reagent, HTIB. All the numerous results described in this article have been divided into three main groups 2A, 2B and 2C. The first group (2A) embraces syntheses of heterocycles based on the reactions of α -tosyloxy ketones which are analogous to α -halogeno ketones. The syntheses of various aromatic heterocyclic compounds based on the miscellaneous approaches are included in group 2B. The third group (2C) deals with the syntheses of reduced heterocyclic compounds. These main groups are subdivided into various subgroups/sections according to the individual category of heterocycles.

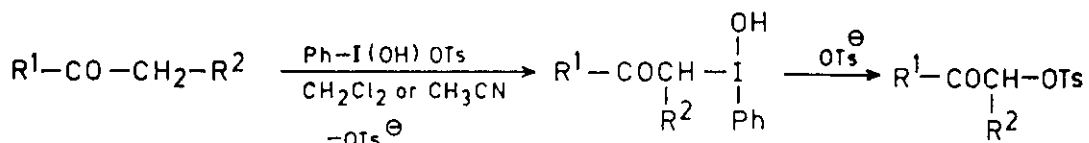
2. DISCUSSION

2A : Syntheses of heterocycles and bridgehead heterocycles based on the similarity between α -tosyloxy ketones and α -halogeno ketones

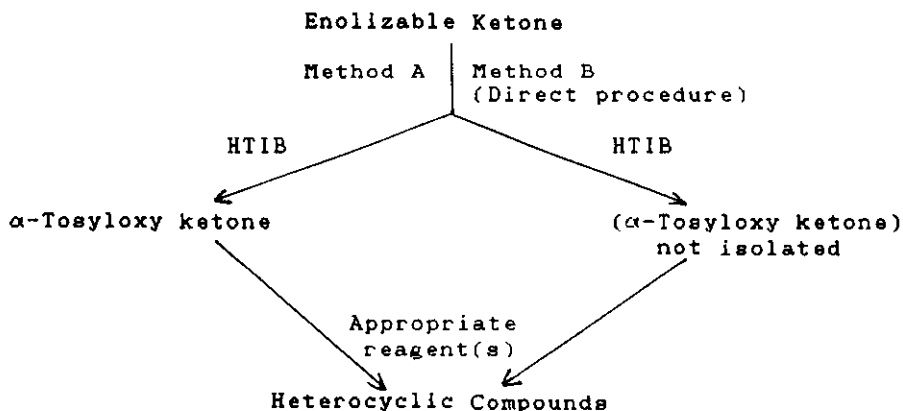
The use of α -halogeno ketones (HK) in organic synthesis in general and in the synthesis of heterocyclic compounds in particular is the most common and widely accepted approach.¹⁰ Although this approach is still a method of choice to obtain a wide variety of large number of heterocyclic compounds, the main disadvantage and difficulty in using HK is their high lachrymatory and toxic properties. As a consequence, efforts have been made to search for alternatives of the methodology involving HK. The work presented in this part is directed towards the fulfilment of this task. A simple and quite general approach based on the observed analogy between α -halogeno ketones and α -tosyloxy ketones (TK) has been introduced. This observation of analogy between TK, which are crystalline solids, easy to isolate and handle, and readily accessible by HTIB oxidation of enolizable ketones¹¹ (Scheme 1), and HK provides a safer and superior alternative of HK. Since it is generally not necessary to isolate TK, they are generated in situ and then treated with appropriate reagents to furnish

the desired heterocyclic compounds by a one pot procedure (Method B, Scheme 2). The results on the individual class of heterocyclic compounds using this approach are presented in Schemes 3-10 (2A.1-2A.8)

Scheme 1

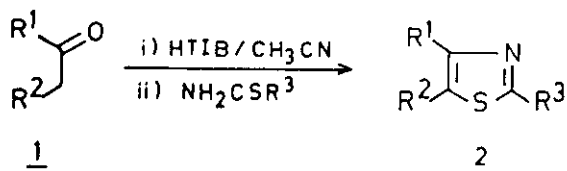


Scheme 2. General scheme for synthesizing heterocyclic compounds



2A.1. 2-Amino/substituted amino and related thiazoles (Modified Hantzsch thiazole synthesis)

Scheme 3

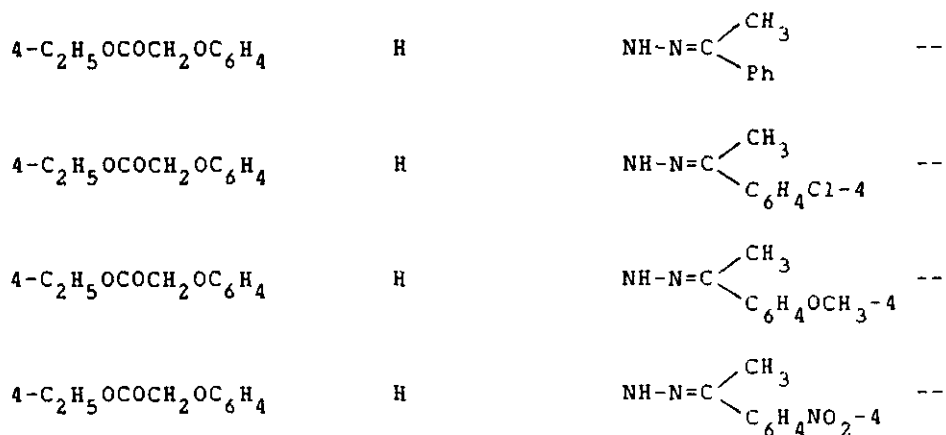


R^1	R^2	R^3	Ref.
Ph	H	NH_2	12
Ph	$COCH_3$	NH_2	12

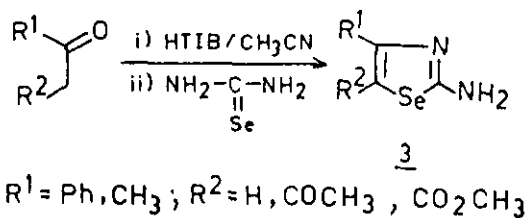
(continued)

CH ₃	COCH ₃	NH ₂	12
CH ₃	CO ₂ CH ₃	NH ₂	12
2-BzOC ₆ H ₄	H	NH ₂	13
2-BzOC ₆ H ₄	H	NHPh	13
2-BzOC ₆ H ₄	H	NHC ₆ H ₄ Cl-4	13
2-BzOC ₆ H ₄	H	NHC ₆ H ₄ CH ₃ -4	13
2-BzOC ₆ H ₄	H	NHC ₆ H ₄ OCH ₃ -4	13
2-BzO-5-ClC ₆ H ₃	H	NH ₂	13
2-BzO-5-ClC ₆ H ₃	H	NHC ₆ H ₄ Cl-4	13
2-BzO-5-ClC ₆ H ₃	H	NHC ₆ H ₄ OCH ₃ -4	13
2-BzO-5-CH ₃ OC ₆ H ₃	H	NH ₂	13
2-BzO-5-CH ₃ OC ₆ H ₃	H	NHPh	13
2-BzO-5-CH ₃ OC ₆ H ₃	H	NHC ₆ H ₄ Cl-4	13
2-BzO-5-CH ₃ OC ₆ H ₃	H	NHC ₆ H ₄ CH ₃ -4	13
2-BzO-5-CH ₃ OC ₆ H ₃	H	NHC ₆ H ₄ OCH ₃ -4	13
2-BzO-5-CH ₃ OC ₆ H ₃	H	CH ₃	13
2-BzO-5-CH ₃ OC ₆ H ₃	H	Ph	13
4-ClC ₆ H ₄	H	2-thienyl	14
4-BrC ₆ H ₄	H	2-thienyl	14
4-FC ₆ H ₄	H	2-thienyl	14
4-CH ₃ C ₆ H ₄	H	2-thienyl	14
4-CH ₃ OC ₆ H ₄	H	2-thienyl	14
4-NO ₂ C ₆ H ₄	H	2-thienyl	14
2-thienyl	H	Ph	14
2-thienyl	H	4-ClC ₆ H ₄	14
2-thienyl	H	4-CH ₃ OC ₆ H ₄	14
2-thienyl	H	2-thienyl	14
4-C ₂ H ₅ OCOCH ₂ OC ₆ H ₄	H	NH-N=C $\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$	--

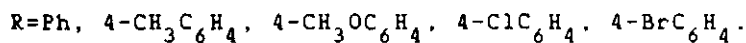
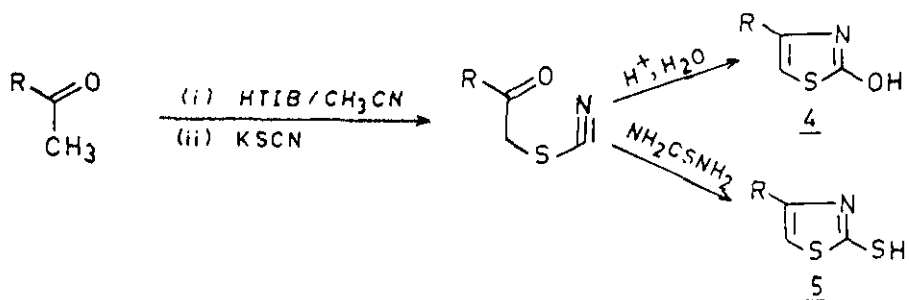
(continued)

2A.2. Selenazoles¹²

Scheme 4

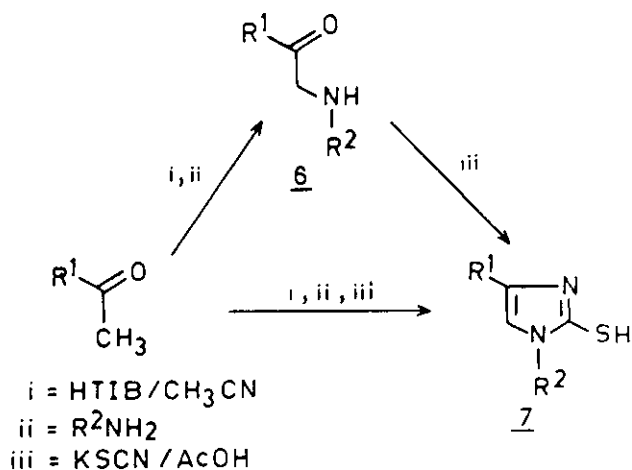
2A.3. 2-Hydroxy- and 2-mercaptothiazoles¹⁵

Scheme 5



2A.4. 2-Mercaptoimidazoles¹⁶ (Modified Marckwald's synthesis)

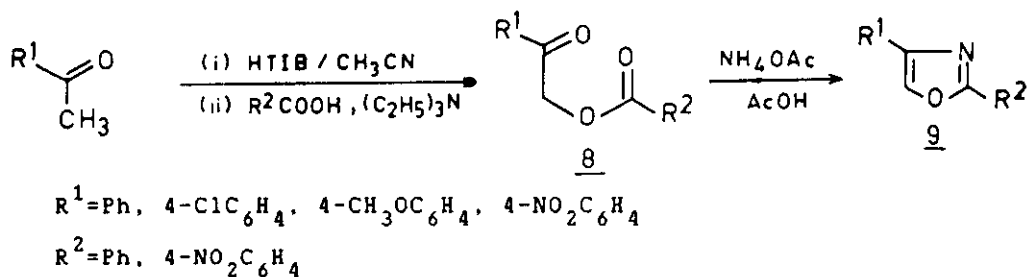
Scheme 6



R ¹	R ²	R ¹	R ²
Ph	Ph	C ₆ H ₄ OCH ₃ -4	C ₆ H ₄ OCH ₃ -4
Ph	C ₆ H ₄ OCH ₃ -4	C ₆ H ₄ NO ₂ -4	Ph
C ₆ H ₄ Cl-4	C ₆ H ₄ OCH ₃ -4	2-thienyl	Ph
C ₆ H ₄ Cl-4	C ₆ H ₄ CH ₃ -4	2-thienyl	C ₆ H ₄ Cl-4
C ₆ H ₄ Cl-4	C ₆ H ₄ OCH ₃ -4	2-thienyl	C ₆ H ₄ Br-4
C ₆ H ₄ Br-4	C ₆ H ₄ CH ₃ -4	2-thienyl	C ₆ H ₄ F-4
C ₆ H ₄ Br-4	C ₆ H ₄ OCH ₃ -4	2-thienyl	C ₆ H ₄ CH ₃ -4
C ₆ H ₄ OCH ₃ -4	Ph	2-thienyl	C ₆ H ₄ OCH ₃ -4
C ₆ H ₄ OCH ₃ -4	C ₆ H ₄ CH ₃ -4		

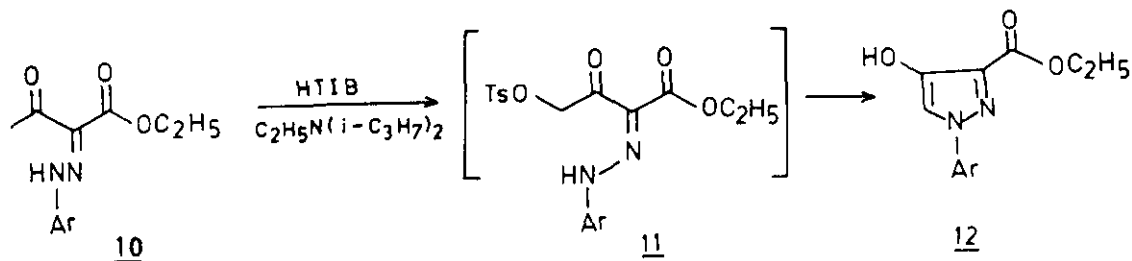
2A.5. 2,4-Diaryloxazoles via α-aryloxyacetophenones

Scheme 7



2A.6. Pyrazoles¹⁷

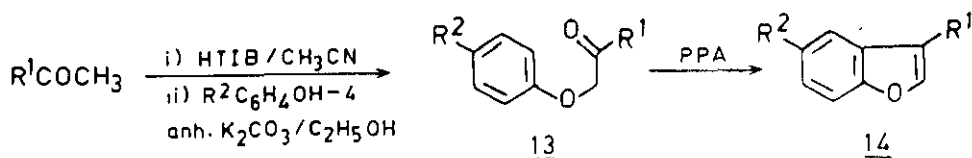
Scheme 8



Ar = Ph, 4-BrC₆H₄, 2-NO₂C₆H₄, 4-NO₂C₆H₄, 3,5-Cl₂C₆H₃, 3,5-Br₂C₆H₃,
 2,4,6-Cl₃C₆H₂, 2,4,6-Br₃C₆H₂.

2A.7. Benzofurans via α -aryloxyacetophenones

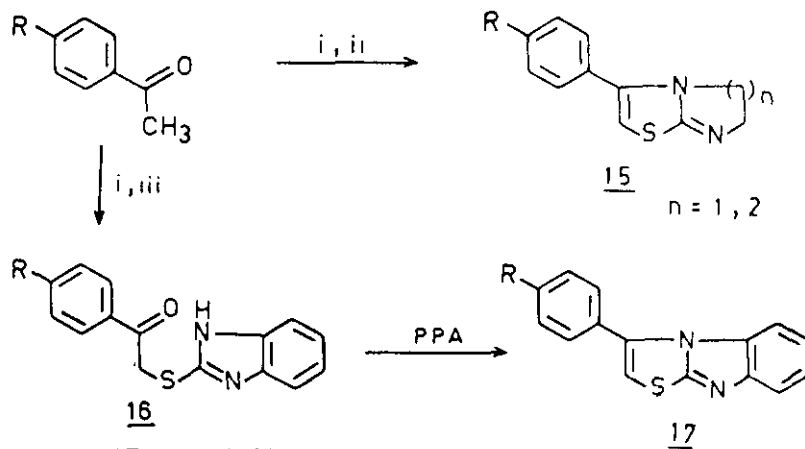
Scheme 9



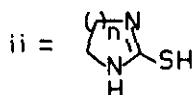
R¹ = Ph, 4-CH₃C₆H₄, 4-CH₃OC₆H₄, 4-BrC₆H₄; R² = H, CH₃, NO₂.

2A.8. Bridgehead heterocycles^{18,19}

Scheme 10



i = HTIB/CH₃CN



iii = 2-mercaptobenzimidazole

R = H, Cl, Br, CH₃,
OCH₃, NO₂

It must be noted that scheme 3 provides a useful modification of a well known Hantzsch thiazole synthesis²⁰ whereas Scheme 6 offers a valuable modification over Markwald's synthesis of 2-mercaptoimidazoles²¹ (7). The methodology is also applicable for synthesizing 4-(2-thienyl)thiazoles (2; R¹=2-thienyl; R²=H; R³=aryl, 2-thienyl) and imidazoles (7; R¹=2-thienyl; R²=aryl) some of which are associated with impressive level of phototoxicity against a variety of biological systems.²² It is further noteworthy that intermediates (6,²³ 8, 13 and 16) involved in these Schemes (6,7,9 and 10) are important precursors in organic synthesis and can be prepared by using the same methodology.

Working on the similar lines, bridgehead heterocycles such as 15 and 17 have also been synthesized successfully. This (Scheme 10) clearly illustrates the advantage and scope of this approach for obtaining bridgehead heterocyclic systems.

2B. : Syntheses of heterocycles (mainly aromatic) based on miscellaneous Approaches

2B.1. 2-Aroylcoumaran-3-ones²⁴

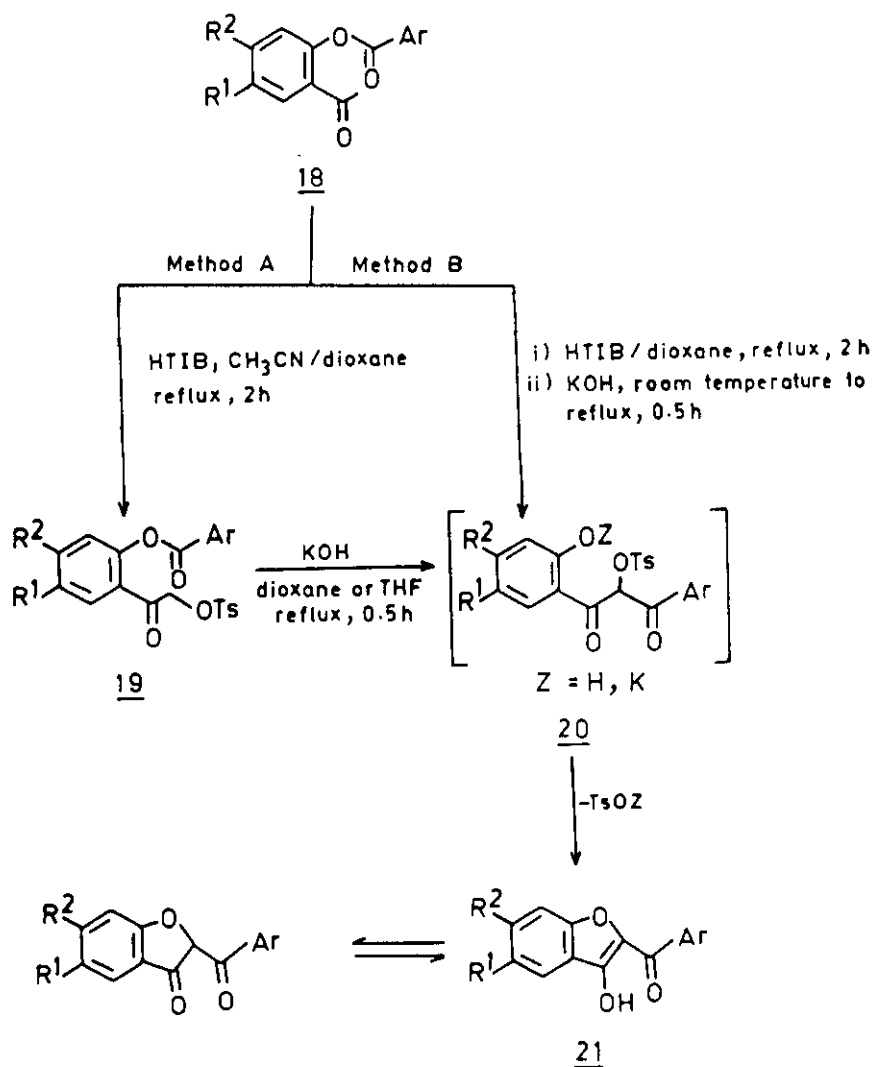
Hypervalent iodine oxidation of *o*-aroyloxyacetophenones (18) with HTIB, followed by Baker-Venkatraman rearrangement (BVR) of the resultant *o*-aroyloxy- α -tosyloxyacetophenones (19), with potassium hydroxide consisting of two experimental methods (A and B), provided a convenient and useful synthesis of 2-aroylcoumaran-3-ones (21) (Scheme 11). It may be noted that this offers an alternative of existing procedures involving BVR of *o*-aroyloxy-2- α -halogenoacetophenones²⁵⁻²⁷ or cyclization of α -halogenated *o*-hydroxyaryl β -diketones.^{28,29}

2B.2. Important interconversions in flavonoids

2B.2.a. Flavanones (22) \longrightarrow Isoflavones (25)³⁰

The oxidation of flavanones (22) with HTIB in acetonitrile/propionitrile at reflux temperature does not afford the expected 3-tosyloxyflavanones

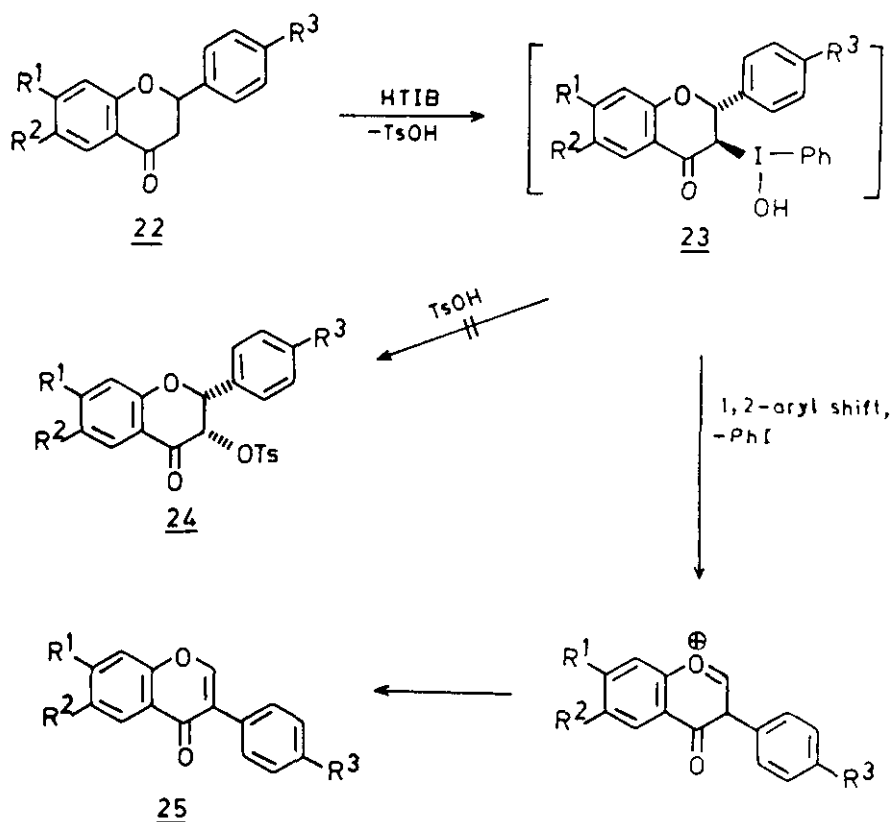
Scheme 11



<u>18-21</u>	<u>R¹</u>	<u>R²</u>	<u>Ar</u>	<u>18-21</u>	<u>R¹</u>	<u>R²</u>	<u>Ar</u>
<u>a</u>	H	H	Ph	<u>d</u>	H	OCH ₃	Ph
<u>b</u>	Cl	H	Ph	<u>e</u>	H	OCH ₃	C ₆ H ₄ OCH ₃ -4
<u>c</u>	Cl	CH ₃	Ph	<u>f</u>	Cl	H	C ₆ H ₄ OCH ₃ -4

(24). Instead, a 1,2-shift (23 → 25) of the aryl group to α-carbon atom of the ketone function occurs, thus constituting a novel route to the iso-flavones (25) (Scheme 12)

Scheme 12

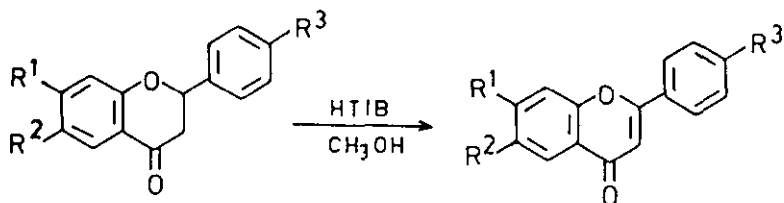


<u>22-25</u>	<u>R¹</u>	<u>R²</u>	<u>R³</u>	<u>22-25</u>	<u>R¹</u>	<u>R²</u>	<u>R³</u>
<u>a</u>	H	H	H	<u>e</u>	H	Cl	CH ₃
<u>b</u>	H	H	OCH ₃	<u>f</u>	H	CH ₃	Cl
<u>c</u>	H	Cl	H	<u>g</u>	OCH ₃	OCH ₃	H
<u>d</u>	H	Cl	OCH ₃				

2B.2.b. *Flavanones (22)* \longrightarrow *Flavones (26)*³¹

The use of methanol in place of acetonitrile/propionitrile as solvent in the reaction of 22 with HTIB results in the formation of flavones (26). This transformation is a new and simple approach for the dehydrogenation of 22 (Scheme 13).

Scheme 13

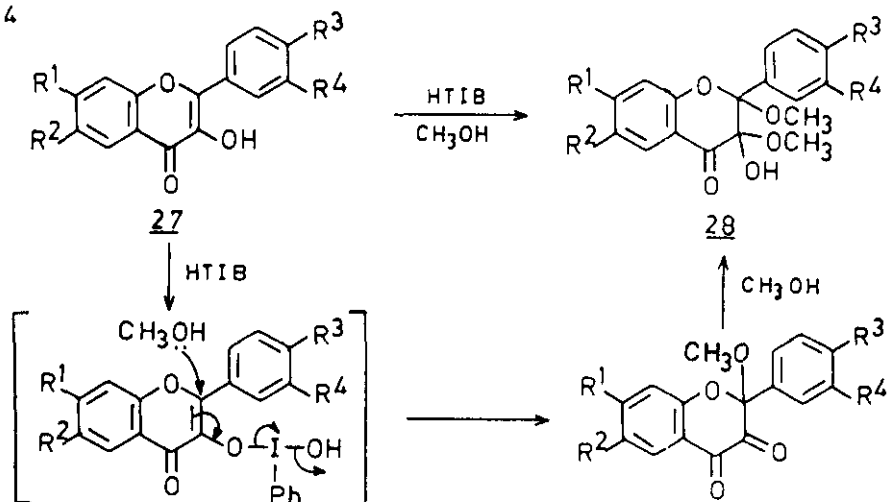


<u>22, 26</u>	<u>R¹</u>	<u>R²</u>	<u>R³</u>	<u>22, 26</u>	<u>R¹</u>	<u>R²</u>	<u>R³</u>
<u>a</u>	H	H	H	<u>d</u>	Cl	H	Cl
<u>b</u>	Cl	H	H	<u>e</u>	H	H	Cl
<u>c</u>	Cl	H	OCH ₃	<u>f</u>	CH ₃	H	Cl
				<u>g</u>	OCH ₃	H	OCH ₃

2B.2.c. *Flavonols (27) → 2,3-Dimethoxy-3-hydroxyflavanones (28)*^{32, 33}

The oxidation of flavonols (27) with HTIB in methanol proceeds with the introduction of two methoxy groups into the carbon-carbon double bond and 2,3-dimethoxy-2-hydroxyflavanones (28) are obtained (Scheme 14). In some respects, this transformation is analogous to the ditosyloxylation of alkenes with HTIB³⁴ and is an example of a solvohyperiodination reaction. Kapoor *et al.*³³ extended the application of this method for the transformation of 6-propionylflavonols (27g-j → 28g-j). It is interesting to mention that based on the observed analogy between I(III) reagents and Tl(III) salts,^{33, 35} Kapoor *et al.*³⁶⁻³⁸ reported the similar results (Schemes 12-14) with Tl(III) reagents.

Scheme 14

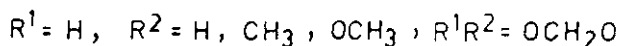
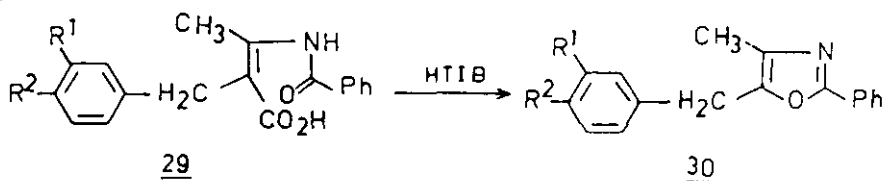


<u>27,28</u>	<u>R¹</u>	<u>R²</u>	<u>R³</u>	<u>R⁴</u>	<u>27,28</u>	<u>R¹</u>	<u>R²</u>	<u>R³</u>	<u>R⁴</u>
<u>a</u>	H	H	H	H	<u>f</u>	H	H	Cl	H
<u>b</u>	OCH ₃	H	H	H	<u>g</u>	H	COC ₂ H ₅	H	H
<u>c</u>	H	H	OCH ₃	H	<u>h</u>	H	COC ₂ H ₅	Cl	H
<u>d</u>	OCH ₃	H	OCH ₃	H	<u>i</u>	H	COC ₂ H ₅	CH	H
<u>e</u>	H	H	OCH ₃	OCH ₃	<u>j</u>	H	COC ₂ H ₅	OCH ₃	H

2B.3. 2-Aryl-4-methyl-5-substituted oxazoles³⁹

Bhaduri et al.³⁹ have reported the preparation of 30 by HTIB induced ring closure of enamine carboxylic acids (29) (Scheme 15).

Scheme 15

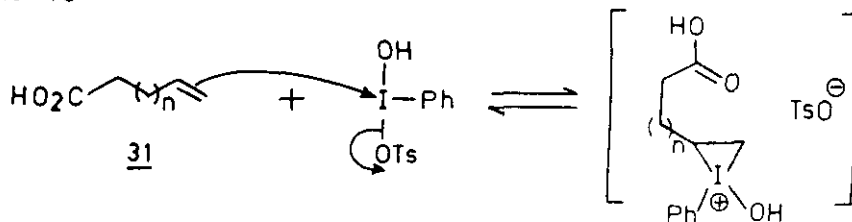


2C. Synthesis of Reduced Heterocyclic Systems

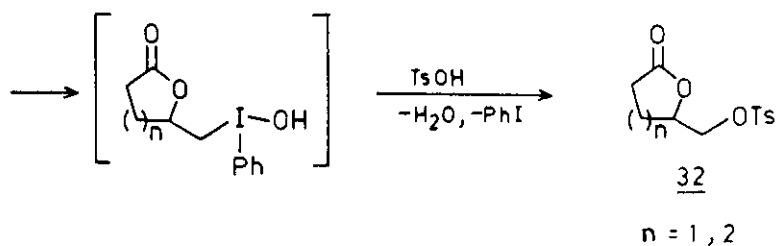
2C.1. Tosyloxylactones and bislactones by intramolecular participation of the carboxylic group

The oxidation of alkenes with HTIB gives ditosyloxyalkanes.³³ When selected alkenoic acids (31) are treated with HTIB in CH₂Cl₂, tosyloxylactones (32) are resulted, a reaction involving the capture of one end of carbon-carbon double bond with the tosylate ion and the other end with the carboxyl function of the substrate⁴⁰ (Scheme 16).

Scheme 16

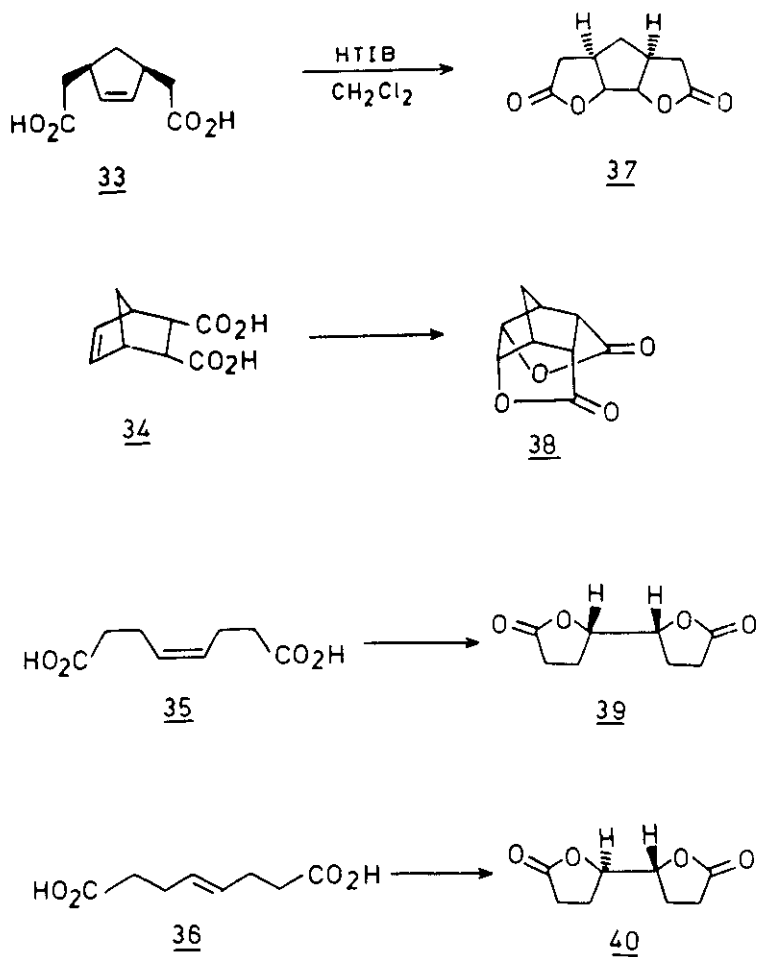


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The treatment of alkenedioic acids (33-36) with HTIB leads to the stereospecific production of respective bislactones (37-40)⁴¹ (Scheme 17).

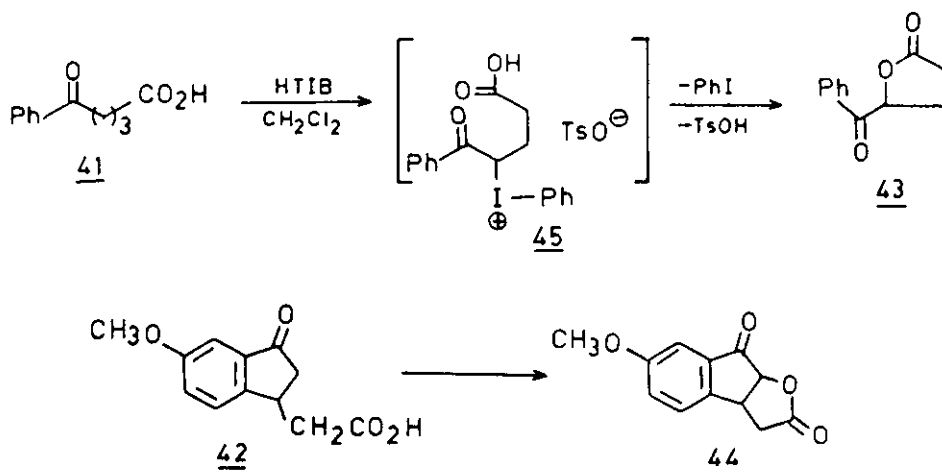
Scheme 17



2C.2. Oxolactones by intramolecular participation of the carboxyl group in the oxidation of ketones

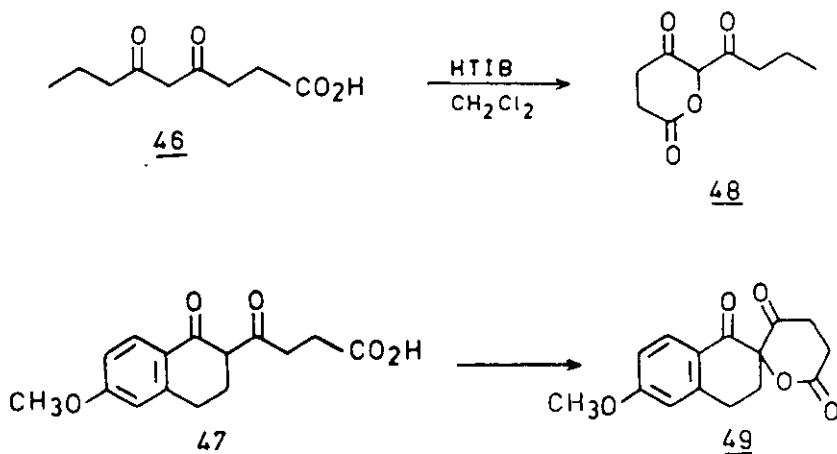
5-Oxocarboxylic acids (41, 42) react with HTIB in CH_2Cl_2 to give oxolactones (43, 44)⁴² (Scheme 18) by intramolecular participation of $-\text{COOH}$ group (45 \rightarrow 43).

Scheme 18



When 4,6-dioxocarboxylic acids (46, 47) are the substrates, dioxo- δ -lactones (48, 49) are obtained (Scheme 19).

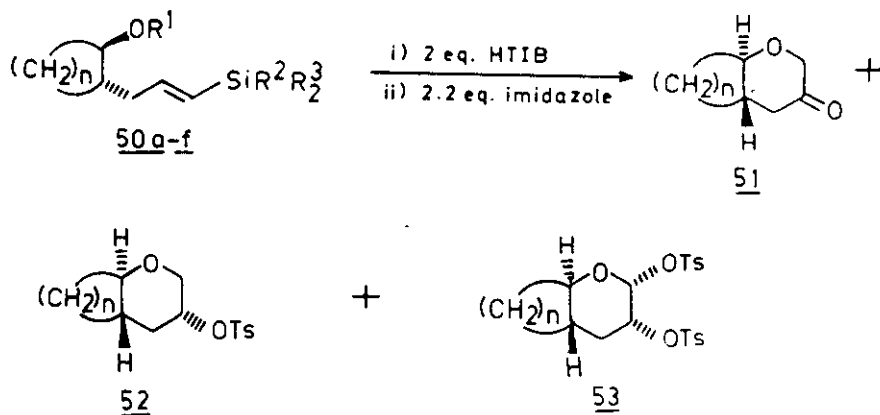
Scheme 19



2C.3. Pyran-3-ones and tetrahydropyrans⁴³

The silyl substituted δ,ϵ -unsaturated alcohols (50) undergo ring closure to give pyran-3-ones (51) as well as tosyloxy substituted tetrahydropyrans (52, 53) (Scheme 20).

Scheme 20

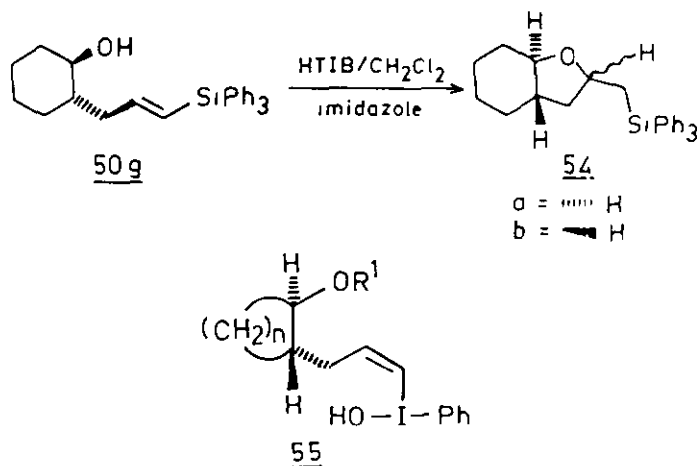


Substrate		Product ratio						
<u>50</u>	<u>n</u>	<u>R¹</u>	<u>R²</u>	<u>R³</u>	<u>51</u>	<u>52</u>	<u>53</u>	Total % yield
<u>a</u>	3	H	CH ₃	CH ₃	>10	1	1	15
<u>b</u>	4	H	CH ₃	CH ₃	3	1	0.5	87
<u>c</u>	4	CH ₃	CH ₃	CH ₃	3	1	0.5	68
<u>d</u>	4	Bn	CH ₃	CH ₃	3	1	0.5	56
<u>e</u>	4	Si(CH ₃) ₂ Thex	CH ₃	CH ₃	3	1	0.6	51
<u>f</u>	4	H	CH ₃	Ph	>5	<0.4	0.4	51
<u>g</u>	4	H	Ph	Ph	--	--	--	62

In alcohols (50f-g) phenyl substituents were used on silicon to assess the effect of electron withdrawing substituents on the regiochemistry of ring closure. Here the diphenylmethylsilyl group leads to the same products as trimethylsilyl substituent in 50a-e, although now the preference for pyran-3-ones (51) is more pronounced (Scheme 20). In contrast, exclusive formation of tetrahydrofurans (54a,b) from triphenylsilyl substituted

alkenol (50g) was observed (scheme 21). This outcome formally corresponds to a stereoselective proton-initiated cyclization leading mainly to the 6,8-cis isomer (54a).⁴⁴

Scheme 21

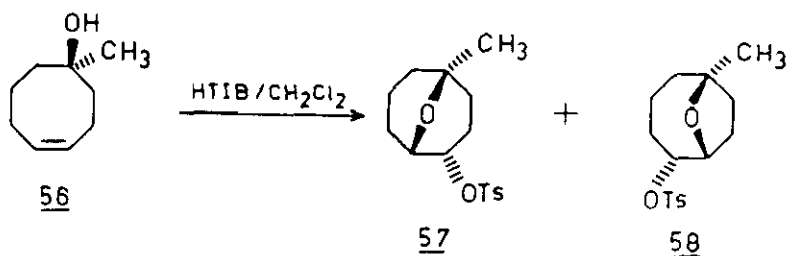


The possible pathways suggested by Schaumann and Kirschning⁴³ involve the Z-vinyliodonium species (55) as intermediate in the formation of 51-54.^{45,46}

2C.4. Tosyloxy-9-oxabicyclononanes by participation of hydroxyl group

HTIB brings about the oxidative cyclization of 1-methyl-4-cyclocten-1-ol (56) in dichloromethane to form a mixture (55% yield) of the tosyloxy-9-oxabicyclononanes (57,58).⁴⁷ Although the reaction shows poor regioselectivity, the addition to the double bond proceeds with high trans-stereoselectivity (Scheme 22).

Scheme 22



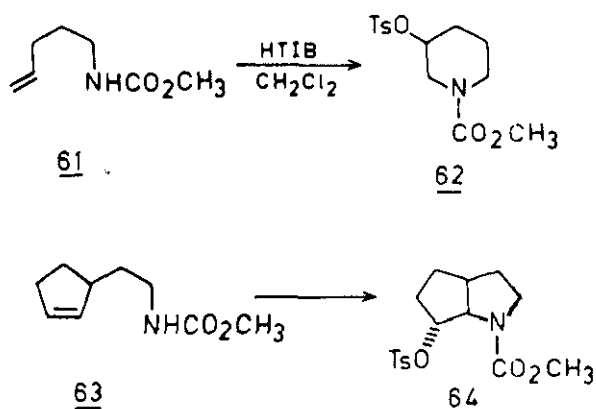
The stereochemistry has been rationalized by the intermediate production of the trans iodonium species (59 and its regio isomer) from an initially formed bridged periodonium ion and its collapse to the bridged oxonium species (60) prior to the introduction of the tosyloxy ligand.⁴⁷



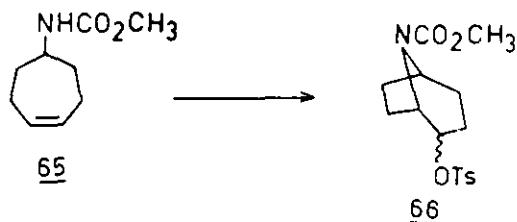
2C.5. N-Methoxycarbonyl-3-tosyloxypiperidine and related nitrogen heterocyclic compounds by participation of carbamate nitrogen

The oxidation of carbamate (61) with HTIB in dichloromethane leads to the formation of *N*-methoxycarbonyl-3-tosyloxypiperidine (62) by intramolecular participation of the nitrogen atom of the carbamate function. The carbamates (63) and (65) on similar reaction afford 64 and 66, respectively (Scheme 23).

Scheme 23

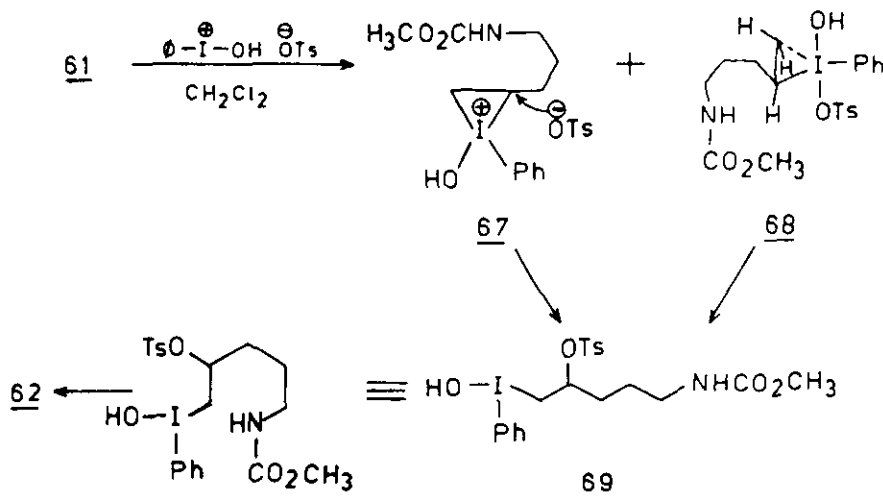


(continued)



The plausible pathways outlined in Scheme 24 (for the conversion **61** \rightarrow **62**) involve the formation of intermediate (**69**), resulted from the selective introduction of tosyloxy ligand at secondary carbon in cyclic hypervalent iodine species such as **67** and **68**. Finally intramolecular participation of the nitrogen atom of the carbamate results in carbon-nitrogen bond formation to give the product (**62**) (Scheme 24).

Scheme 24



3. CONCLUSION

It is evident from the results presented in this article that the use of HTIB has simplified the syntheses of large number and a wide variety of heterocyclic compounds including bridgehead heterocycles. Following concluding remarks will further elaborate the advantages and significance of these HTIB mediated processes :

(i) There exists the possibility of providing a superior replacement of α -halogenoketones, very commonly and widely used precursors particularly in heterocyclic compounds and in organic synthesis in general, by α -tosyloxyketones (Part A).

(ii) Experimentation generally involves one pot simple procedures and yields of the products are mostly better than the existing methods. A further modification from our lab. simplifying the experimental procedure consists of the generation of HTIB in situ by adding a solution of 4-TsOH in CH_3CN to a suspension of iodobenzene diacetate in CH_3CN .

(iii) Some of the thallium (III) salts (highly toxic reagents) based syntheses can also safely be done by using I(III) reagent. Further work in this regard is still demanded.

(iv) Iodobenzene produced quantitatively in all experiments can be recycled to hypervalent iodine reagents.

(v) The new syntheses based on HTIB reagent are quite general. But some exceptions of failure have also been noted. This again reveals the necessity of further investigations to study the full scope of the newly disclosed reactions and observations dealing with comparative reactivity of α -tosyloxyketones and α -halogenoketones. Initial qualitative data on the reactions done so far indicate that the reactivity of TK is slower than HK. Thus, it is hoped that further studies on the reactivity pattern and scope of the reaction will solve many synthetic and mechanistic problems of this area. A particular attention should be directed to extend the similar technique for the synthesis of heterocyclic derivatives with certain structural variations needed for medicinal and biological activities.

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