

Novel reagents of iodine(+III) and sulfur

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Abstract

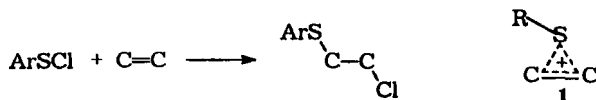
This autoreview covers our results on systematic studies of the phenomenon of competitive covalent binding of nucleofugic anions with the focus of synthetic application and design of novel reagents and reactions.

I. Introduction

Many electrophilic organic processes were formulated as included some ionic intermediates. The classical example is the concept of cyclic “onium ion” intermediate in Ad_E addition to $C=C$ bond [e.g. “bromonium ion” of Roberts and Kimball (1)]. However, in many cases the intermediacy of *pure ions* is not acceptable, and real mechanism has to include sort of *ion-pair* intermediates [see (2-9) and refs therein].

One important question may be posed : is this subtle mechanistic difference important for synthetic purposes? In other words, is it possible to use this mechanistic difference for design of new processes? Our answers was definitely positive and we created the “doping-addition” methodology to regulate chemoselectivity of Ad_E -reactions (2-4).

The electrophilic addition of $RSCl$ to alkenes was selected as reliable model reaction.



It is two-step Ad_E2 -reaction regarded as involving the initial formation of episulfonium ion, **1**. In a view of this concept it was surprising that this reaction usually proceeds (a) without incorporation of external nucleophiles (reaction can be performed in CH_3COOH and CH_3CN), (b) without skeletal rearrangements (4).

One may imagine that other type of intermediates, **2-4**, can be involved (Chart 1).

Chart 1.

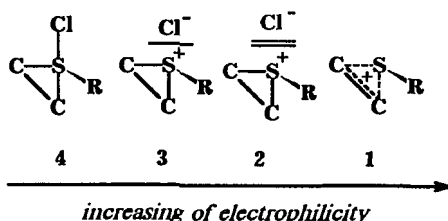
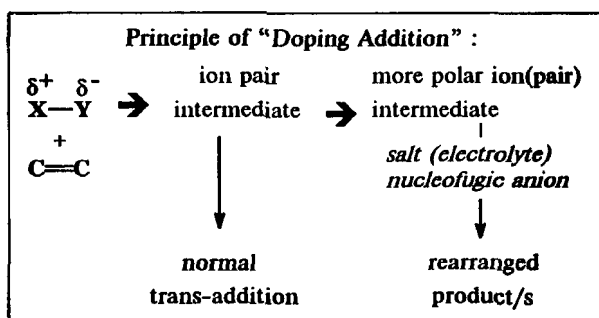
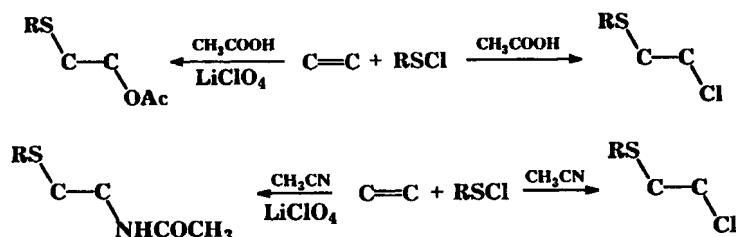


Chart 2



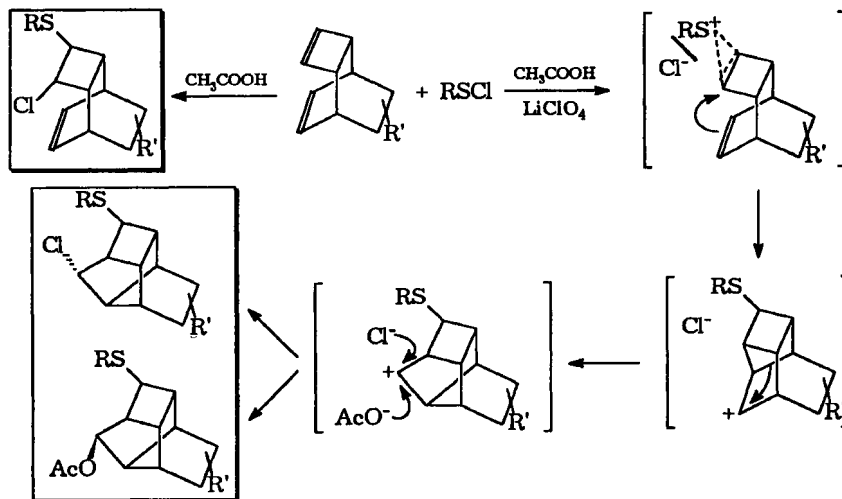
Is it possible to change effective electrophilicity of $RSCl$ by an appropriate change of the reaction conditions? The ion **1** represents the limiting case of the most electrophilic of all other species. Hence, the change of the effective electrophilicity of $RSCl$ with a change in the polarity of media is a test for the involvement of some less polar intermediates of type **2-4**. Thus, we have suggested the idea of “doping effect” : substantially increasing of the effective electrophilicity of $RSCl$ when the reaction is carried out in the presence of strong electrolyte, usually $LiClO_4$ (2,4,7).

It became possible to obtain products of incorporation of the external nucleophiles



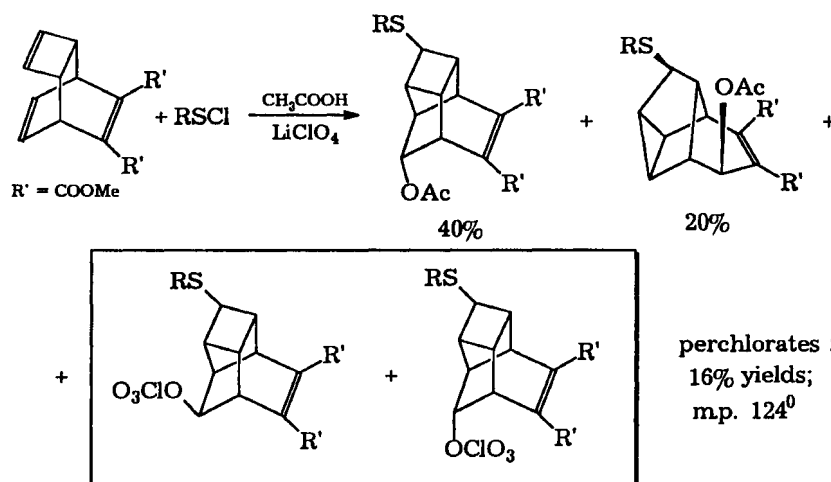
of skeletal rearrangements (Chart 3), of hydride shifts etc (2,6,8).

Chart 3



In 1978 we serendipitously found (in the course of our study of "doping addition") an astonishing phenomenon: the addition of (2-nitrophenyl)sulfonyl chloride to the diester (Chart 4) in acetic acid in the presence LiClO_4 gave the perchlorates together with other products (9). This fact is amazing: ClO_4^- plays the role of a nucleophile which can successfully compete with the chloride ion and even with the solvent.

Chart 4

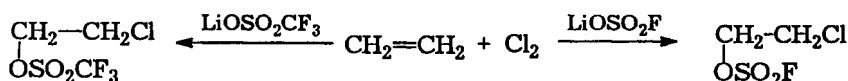
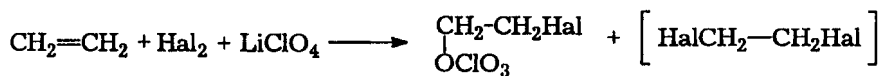


Extension of this work has shown that *competitive covalent binding of nucleofugal anions* (CF_3SO_3^- , ClO_4^- , FSO_3^-) *is the general phenomenon in the processes including carbocationic-like intermediates/transition state*. This phenomenon has extensive theoretical and synthetic applications and ramifications (6,9-29).

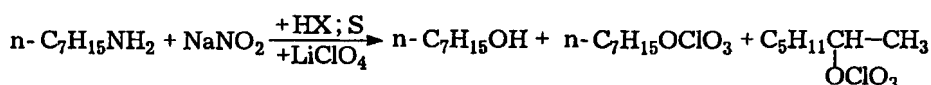
II. Phenomenon of Competitive Nucleophilic Properties of Nucleofugic Anions : Synthetic Application.

This chapter contains selected examples of the novel reactions which were found on the basis of the above phenomenon.

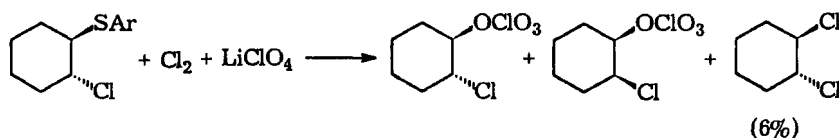
(a) Electrophilic addition to olefins (10,13).



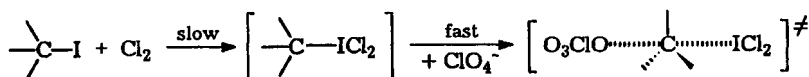
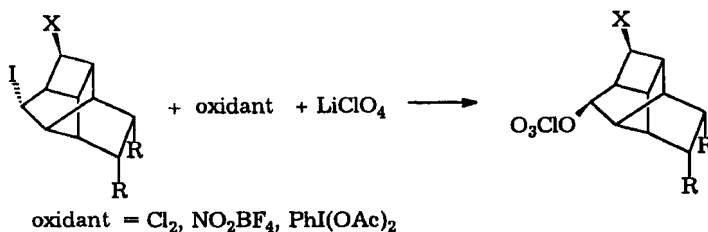
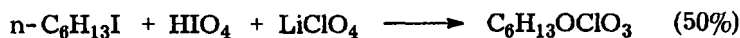
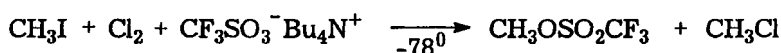
(b) Deamination of amines (11,14).



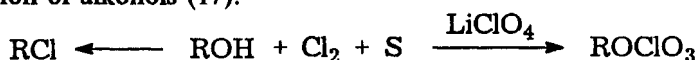
(c) Chlorinolysis of arylsulfides (15).



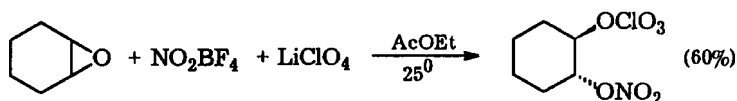
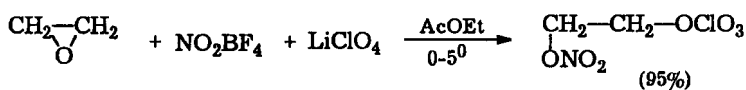
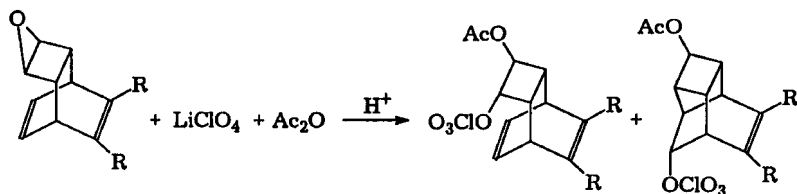
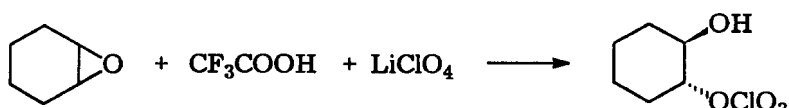
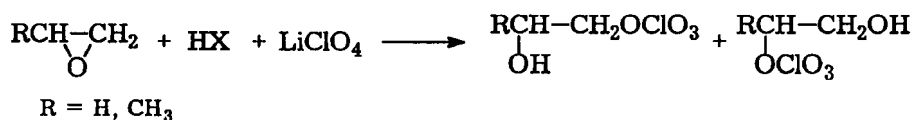
(d) Oxidative deiodination of iodides (11,12,16).



(e) Deoxygenation of alcohols (17).

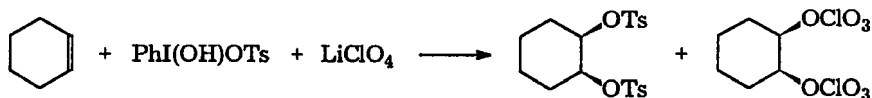


(f) Acid-catalysed epoxide ring opening (14,18).

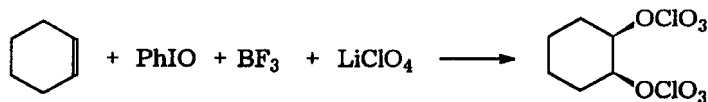


(g) Reactions of iodine(III) reagents with olefins.

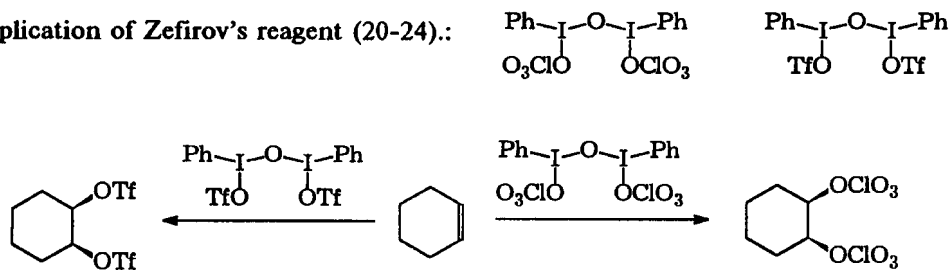
(1.) (19,20).



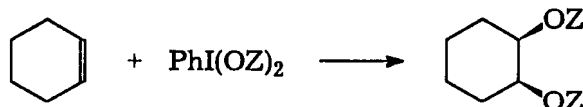
(2.) (20).

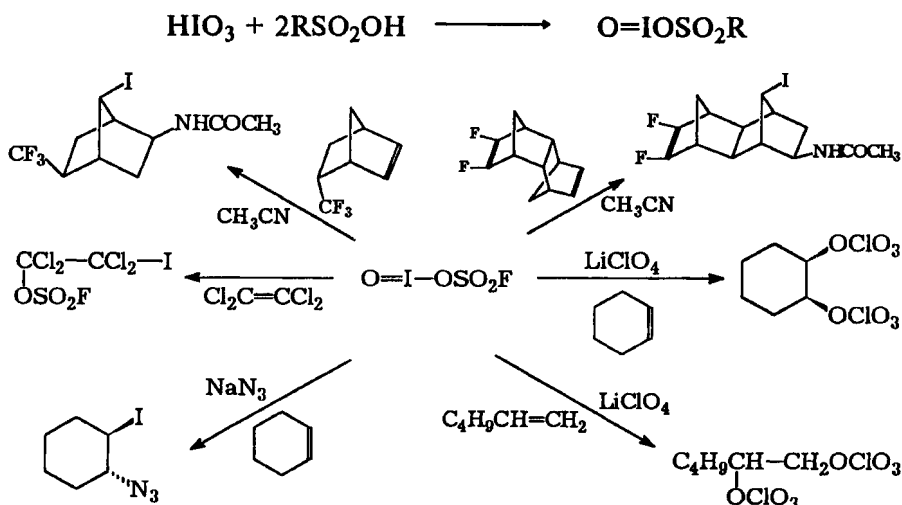


(3.) Application of Zefirov's reagent (20-24):

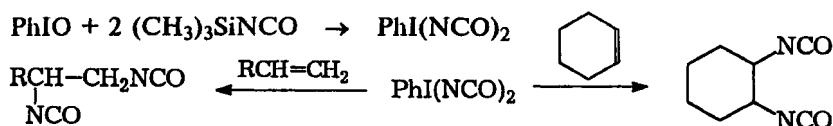


(4.) (20,25,29).

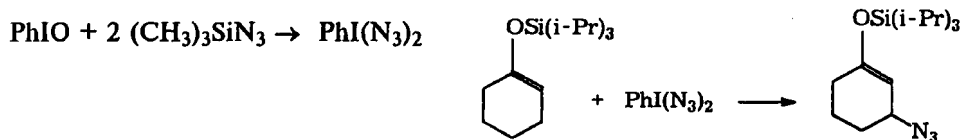


(5.) Iodozyl reagents $O=IOSO_2F$ and $O=IOSO_2CF_3$ (26-28).

(6.)

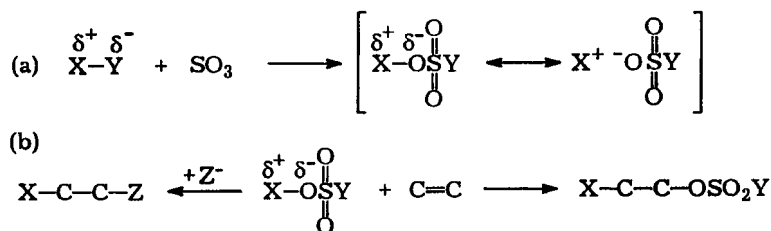


(7.) (29,30).

III. SO_3 -Mediated Electrophilic Addition

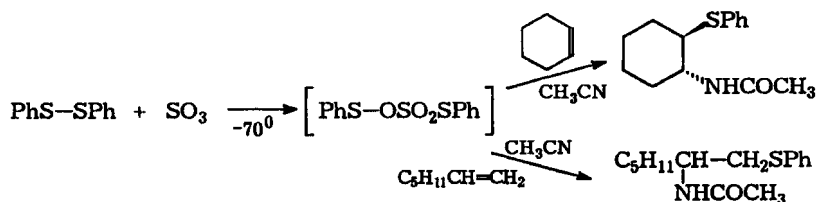
As one of the ramifications of the phenomenon discussed above, we elaborated novel approach to the increasing of electrophilicity of electrophilic reagents. The general idea is the following: SO_3 is capable to insertion reactions into $X^{\delta+}-Y^{\delta-}$ bonds, which leads to new reagents (Chart 5)

Chart 5

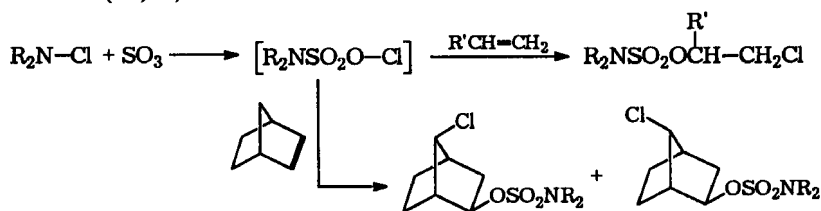


Taking into account clearly pronounced nucleofugic properties of YSO_2O^- anions (super nucleofugic for FSO_3^-) one may expect increased polarization sufficient to design series of novel electrophilic additions (31-40). This statement will be illustrated in this section by selected representative examples.

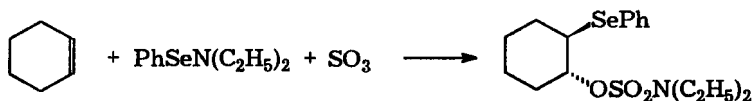
1. S-S bond (36) :



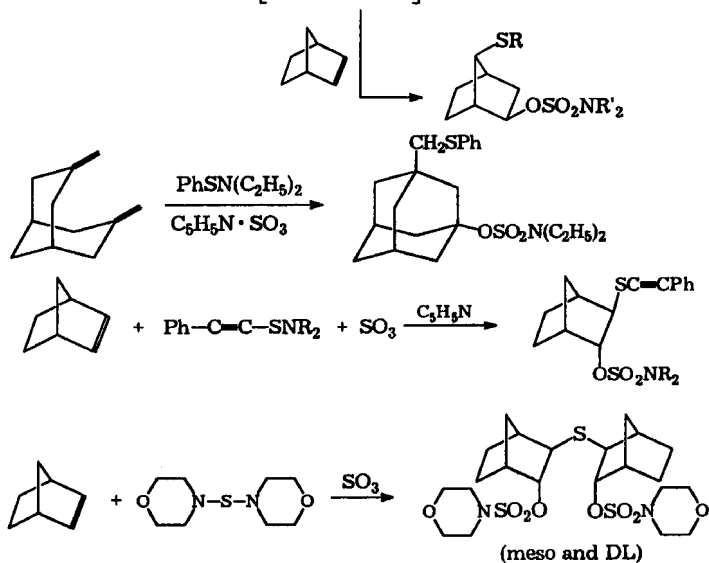
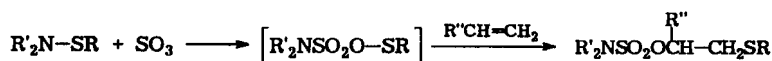
2. N-Cl bond (32,36) :



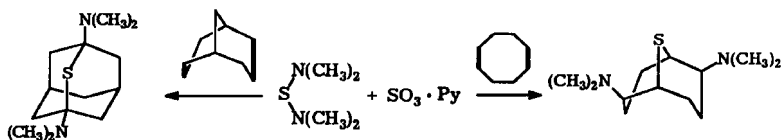
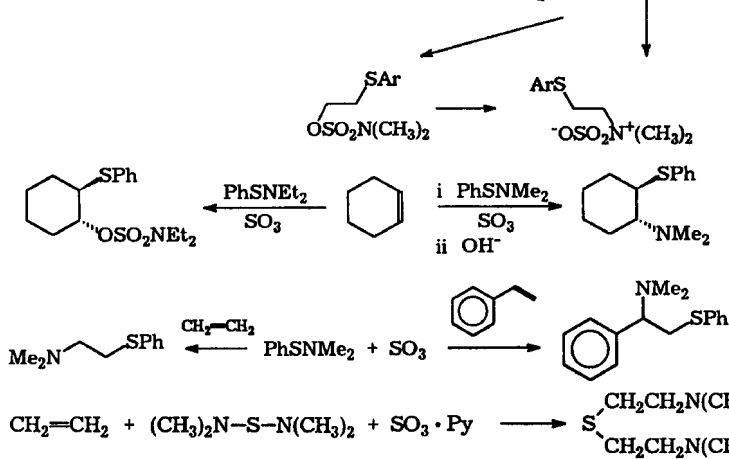
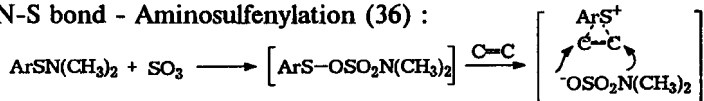
3. N-Se bond (35) :



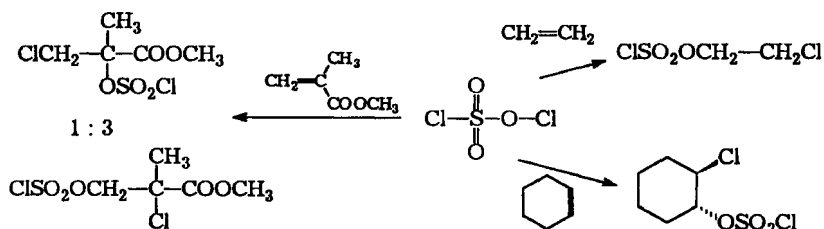
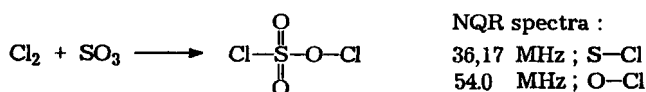
4.1. N-S bond - Addition (36) :



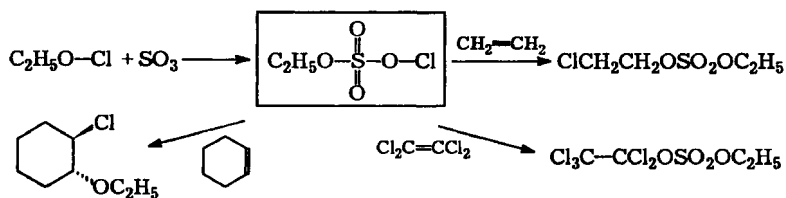
4.2. N-S bond - Aminosulfonylation (36) :



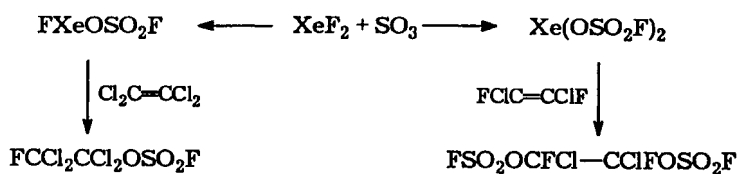
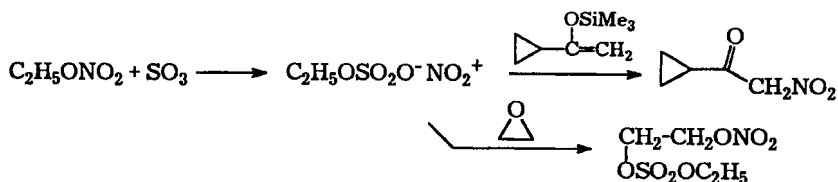
5. Cl-Cl bond (33) :



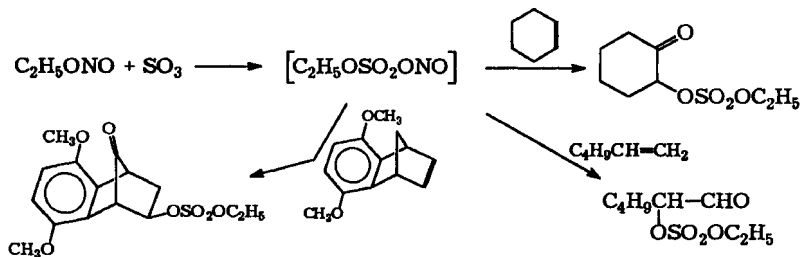
6. O-Cl bond (34) :



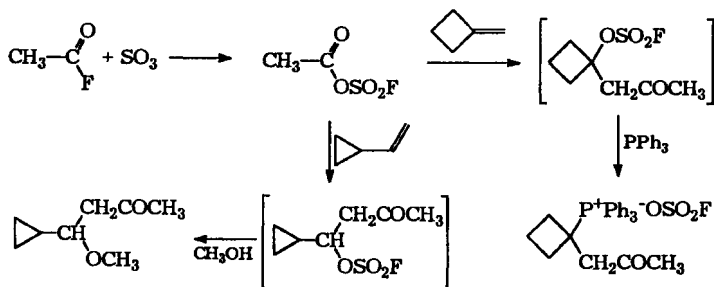
7. Xe-F bond (37) :

8.1. N-O bond : O-NO₂ (38) :

8.2. N-O bond : O-NO (39) :



9. C-F bond (40) :

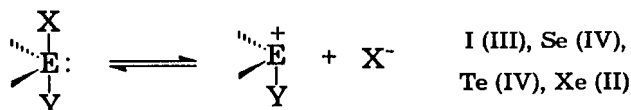


These examples demonstrate large synthetic potential of the suggested approach. Moreover, SO_3 -activation/modification of $\text{X}=\text{Y}$ bonds is also possible, giving extremely interesting new reagents and reactions (20, 31); which consideration however is out of a limit of the present paper.

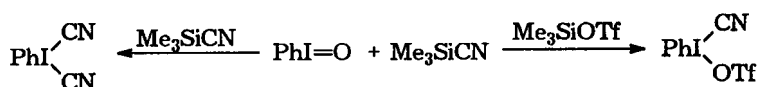
IV. Reactions of Hypervalent Iodine (+III) Reagents

There has been considerable interest in I(+III) containing compounds as reagent in organic synthesis (24). Our interest in these compounds stemmed from our discovery of the phenomenon of competitive binding of nucleofugic anions and we discussed above some of the I(+III) reagents (*e.g.* for *cis*-1,2-ditosylation of olefins). Here we present additional selected examples of the novel I(+III) reagents and their reactions (19,20,25,41-47).

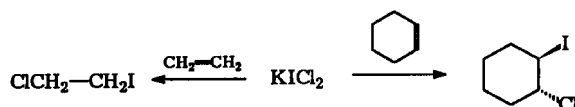
Our main focus was the synthesis of hypervalent elements containing good nucleofugic ligands (41) :



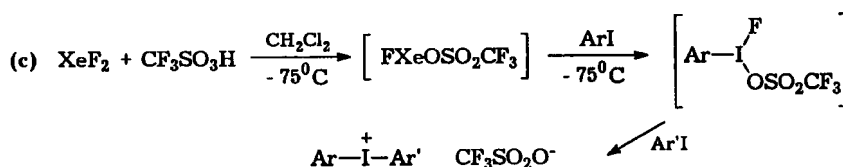
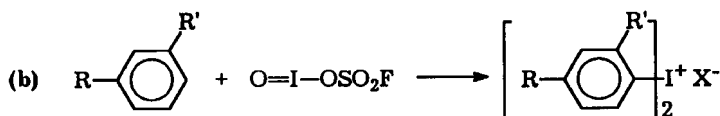
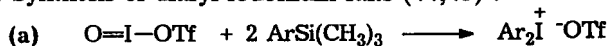
as well as synthesis and application of unusual types of I(+III) compounds. For example, we obtained unusual cyano derivatives (42) :



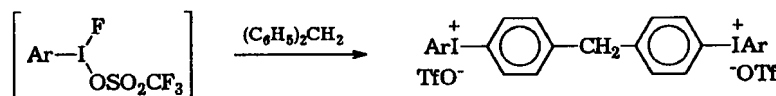
and suggested KICl_2 as versatile iodochlorinating agent (43) :



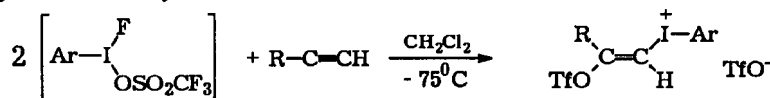
1) Synthesis of diaryl iodonium salts (44,45) :



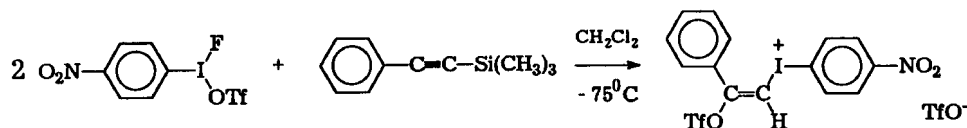
Example:



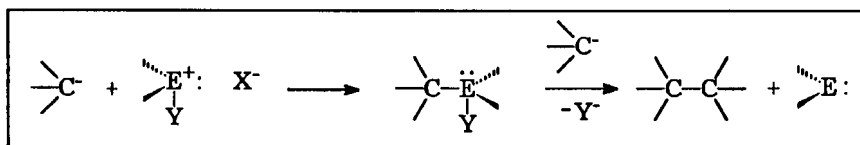
2) Synthesis of vinyl iodonium salts :



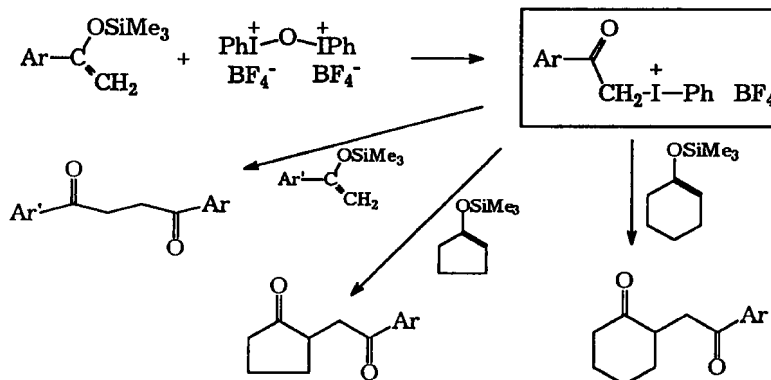
$\text{Ar} = \text{C}_6\text{H}_5$; $\text{R} = \text{C}_4\text{H}_9$, C_8H_{17} , CH_3OCH_2 , ClCH_2 ; $\text{Ar} = p\text{-CH}_3\text{C}_6\text{H}_4$; $\text{R} = \text{C}_4\text{H}_9$, C_8H_{17} , CH_3OCH_2



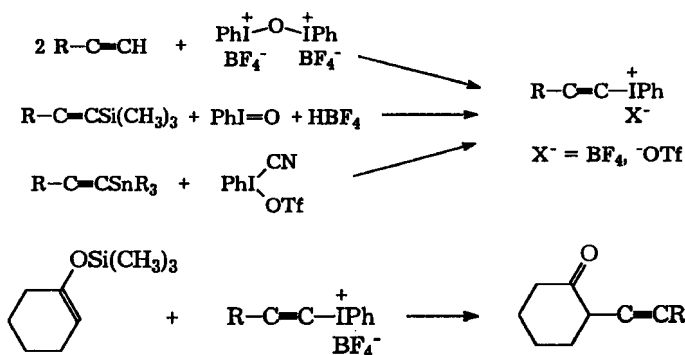
3) General approach to C-C bond formation (41,46,47) :



(a) Synthesis of 1,4-diketones :



(b) Alkynyliodonium salts :



V. Conclusion

In this paper we have attempted shortly to describe some novel reaction and reagents created on the basis of the phenomenon of competitive covalent binding of super-weak nucleophiles in carbocationic processes. We have to emphasize, that the reaction discovered are also of great theoretical significance giving a new look at the fundamental problem of nucleophilicity.

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