HETEROCYCLIC IODONIUM SALTS: PREPARATION, STRUCTURE AND PERSPECTIVES

I.A. Mironova
Scientific advisors – Dr. of Science, Professor M.S. Yusubov[1]; Dr. of Science, Professor V.G. Nenajdenko[2]

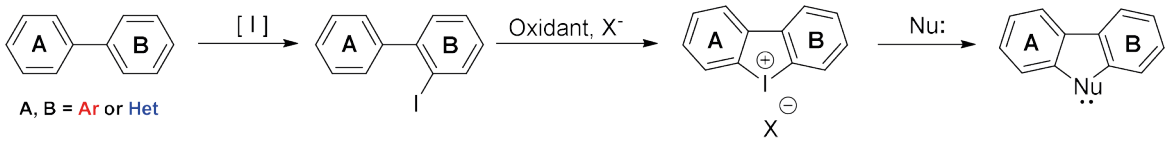
[1]*National Research Tomsk Polytechnic University*
634050, Russia, Tomsk, 30 Lenin Avenue

[2]*Lomonosov Moscow State University*
119991, Russia, Moscow, GSP-1, 1-3 Leninskiye Gory, iam6@tpu.ru

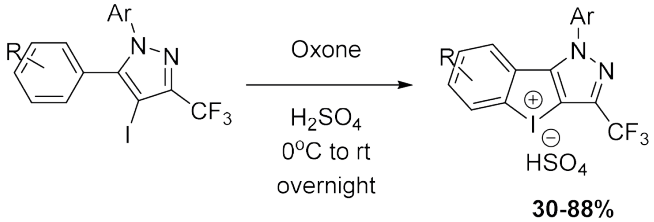
Nowadays hypervalent iodine compounds are universal synthetic reagents with a wide range of applications in science and in the industry [1–3]. Their reactivity is like the one of the derivatives of heavy metals, but hypervalent iodine reagents have eco-benign nature. Diaryliodonium salts are the most known and bright representatives of hypervalent iodine compounds. For the last 5 years, the interest in cyclic and pseudocyclic iodonium salts has skyrocketed due to the advantages of their utilization in organic synthesis, which is concerned with high chemoselectivity and mild reaction conditions [4–5]. The high demand is concerned with the important and irreplaceable utility: the variety of applicable nucleophiles in reactions determines a huge spectrum of practical usage of cyclic iodonium salts in the preparation of annulated carbon- and heterocyclic substances [6–8].

Annulated heterocycles very often can be meeting among natural and bioactive compounds and now relative heterocyclic substances are applied in material science [9] due to their unique structure in particularly interesting electronic and optical properties [10]. In organic photo electronic Sulfur and Selenium play a significant role due to their high polarization that determines properties of the charge transfer process [11]. That is why the development of convenient methods of synthesis of annulated heterocyclic systems containing hypervalent iodine, firstly, will lead to the formation of a novel important class of interesting compounds, secondly, will allow creating of a synthetic methodology of easy-handle preparation of new scope of polyannulated systems, and, finally, will opens the simple approach of functionalization of electron-rich heterocyclic systems (scheme 1).

We have used our previously reported [12] oxidative system with the utilization of eco-friendly Oxone to prepare pyrazole-containing cyclic iodonium salts (scheme 2) with yields up to 88%.



Scheme 1. *Synthesis and perspectives of cyclic iodonium salts*



Scheme 2. *Synthesis of pyrazole-containing cyclic iodonium salts with the use of Oxone-H_2SO_4 system*

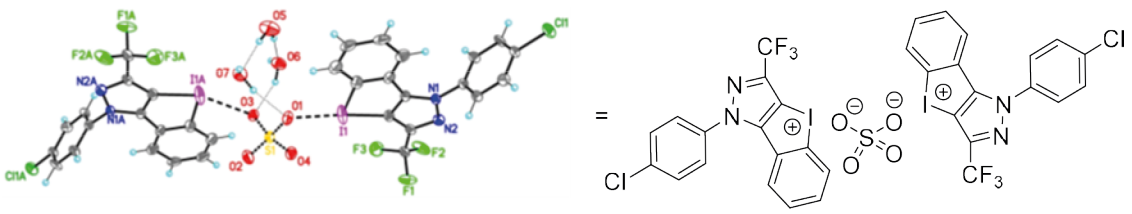


Fig. 1. *X-Ray analysis of pyrazole-containing cyclic iodonium salt*

We have performed X-Ray analysis to investigate the structure of the synthesized salt (Figure 1):

Factly, we shown for the first time double coordination 2 molecules of iodonium salts with sulfate-anion instead of hydrosulfate. Also, it was proved, that the salts indeed have cyclic structure.

Acknowledgements

This work was supported by the Russian scientific foundation (project №21-73-20031).

References

1. *Yoshimura A. et al.// Chem. Rev., 2016. – 116 (5). – 3328.*
2. *Muñiz K. et al.// Adv. Synth. Catal., 2019. – 361. – 2.*
3. *Yusubov M.S. et al.// Resource-Efficient Tech., 2015. – 1. – 49.*
4. *Yoshimura A. et al.// Chem. Eur. J., 2018. – 24 (57). – 15156.*
5. *Postnikov P.S. et al.//Chem. Commun., 2018. – 54. – 10363.*
6. *Vlasenko Y.A. et al. // Chem. Heterocycl. Compd., 2020. – 56 (7). – 854.*
7. *Boelke A. et al. // Org. Lett., 2020. – 22. – 7261.*
8. *Mathew B.P. et al.// Angew. Chem. Int. Ed., 2017. – 56. – 5007.*
9. *Takimiya K. et al. // Acc. Chem. Res., 2014. – 47. – 1493.*
10. *Mishra A. et al.// Chem. Rev., 2009. – 109. – 1141.*
11. *Cinar M.E. et al. // Chem. Rev., 2015. – 115. – 3036.*
12. *Yusubov M.S. et al. // J. Org. Chem., 2013. – 78. – 3767−3773.*

IDENTIFICATION OF THE REGULARITIES OF THE CETANE INFLUENCE ON THE EFFECTIVENESS OF THE DEPRESSANT ADDITIVE

Y.P. Morozova, I.A. Bogdanov
Scientific supervisor – researcher of Division for Chemical Engineering I.A. Bogdanov
Linguistic advisor – researcher of Division for Chemical Engineering I.A. Bogdanov

National Research Tomsk Polytechnic University
634050, Russia, Tomsk, Lenin avenue, 30, yanamorozovaa@mail.ru

The effectiveness of the depressant additives most strongly depends on the hydrocarbon composition of diesel fuel (DF), which is associated with the specific mechanism of interaction depressants with hydrocarbons.

A change in the fractional composition of DF can have a positive and a negative effect on the effectiveness of the depressant additive. It was previously found that with an increase in the proportion of light fractions and the total content of n-paraffins, the effectiveness of the action of depressants decreases [1, 2].

For identification of the regularities of the light n-paraffins effect on the effectiveness of the depressant action, blends of two DF samples (DF 1 and DF 2) with additives (Ad) and similar blends with the addition of cetane and a depressant were prepared, the concentration of cetane in the blends was 1, 3, 5 and 10 % vol. Cetane was chosen as a typical representative of light n-paraffins that make up diesel fuel.

According to the requirements of [3], the cloud point (CP), the pour point (PP), and the cold filter plugging point (CFPP) for all prepared blends were determined.

The change in low-temperature properties when adding different concentrations of cetane to a blend of DF samples with an additive is shown in Figures 1–2.

Based on the results presented in Figures 1–2, it can be seen that the addition of cetane to blends of DF samples with an additive reduces the effectiveness of the additive on CFPP and PP. In regard to CP, the addition of cetane does not have a significant effect on the action of the additive (the changes obtained are within the error of method). The greatest negative effect (increase in temperature by 15 °C) is observed in relation to PP of sample DF 2 with the addition of 5 % vol. cetane. It can also be seen that with an increase in the content of cetane in the blend with the sample DF 1, the negative effect is increase.