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**Korotkikh[1], N.I., Saberov[2], V.Sh., Rayenko[1], G.F.,
Glinyanaya[1], N.V., Knishevitsky[2], A.V., and Shvaika[1], O.P.**

[1] L.M. Litvinenko Institute of Physical, Organic and Coal Chemistry, the NAS of Ukraine, Kyiv
[2] Institute of Organic Chemistry, the NAS of Ukraine, Kyiv

CHEMISTRY OF STABLE CARBENES AND «GREEN» TECHNOLOGIES

The fundamental researches in the chemistry of stable carbenes carried out by the L.M. Litvinenko Institute of Physical, Organic & Coal Chemistry of the NAS of Ukraine (IPOCC) over the last decade and applications in the field of «green» technologies based on the results of these researches have been described. Carbene versions of Claisen ester condensation with the formation of zwitterionic compounds, the Leuckart-Wallach reaction with the autoreduction of carbenoid azolium salts, the Hofmann cleavage of aminocarbene insertion products, induced tandem autotransformation of 1,2,4-triazol-5-ylidenes into 5-amidino-1,2,4-triazoles have been discovered. New carbene reactions of addition, deesterification, oxidation, and complex formation have been found. Effective methods for obtaining stable carbenes and carbenoids have been suggested. New types of carbenes, benzimidazolylidenes, superstable conjugated bis-carbenes, and carbenoids have been synthesized. The existence of hypernucleophilic carbenes has been theoretically predicted and experimentally confirmed. Prospects for the use of carbenes and their derivatives, in particular, carbene complexes of transition metals in the catalysis of organic reactions and the search of biologically active compounds have been outlined.

Keywords: heteroaromatic carbenes, synthesis, properties, transformations, catalysis, biological activity, and «green» chemistry.

Chemistry of stable carbenes as compounds of RR'C: type divalent carbon study has been being studied since the mid-twentieth century [1], but a significant progress in this area was reported after Bertrand (1988) [2—4] and Arduengo (1991) [5] discovered the first stable carbenes, the heterocyclic carbenes and the phosphonylsilylcarbenes. Since chemistry is developing very intensively, the carbenes in both fundamental and applied fields open up new possibilities for the use of these substances in practice [6]. In this review, we will focus only on some aspects of the chemistry of stable carbenes and their derivatives with a description of certain types, properties, and transformations, which are the most promising in terms of application, in particular, for the catalysis of organic reactions and the search for biologically active compounds.

At the early stages of studying the carbenes, their instability in the environment (oxygen, moisture, carbon dioxide) made it impossible to identify their individual compounds. After establishing the fact that the steric factors significantly affect the radical stability, the approach to steric shielding of reaction center as a stabilizing factor has been applied to the carbenes. Therefore, the first carbenes were sterically complicated bis (diisopropylamino) phosphonyltrimethylsylilcarbene and 1,3-di(1-adamantyl)imidazol-2-ylidene. They are much less sensitive to environmental factors as compared with the sterically open structures (although still very active), which enables their dimerization in ethylene derivatives. However, it has been found that not all carbenes are

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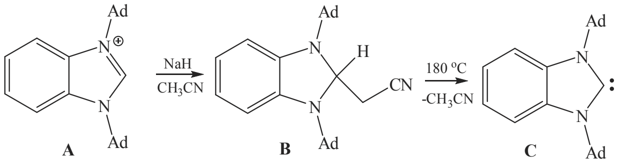
inclined to dimerization; such structures as the imidazole-2-ylidene [7] and 1,2,4-triazole-5-ylidene [8] are stable even in the absence of sterically voluminous substituents due to a strong electronic stabilization.

INCLUSION REACTIONS AND SYNTHESIS OF STABLE CARBENES

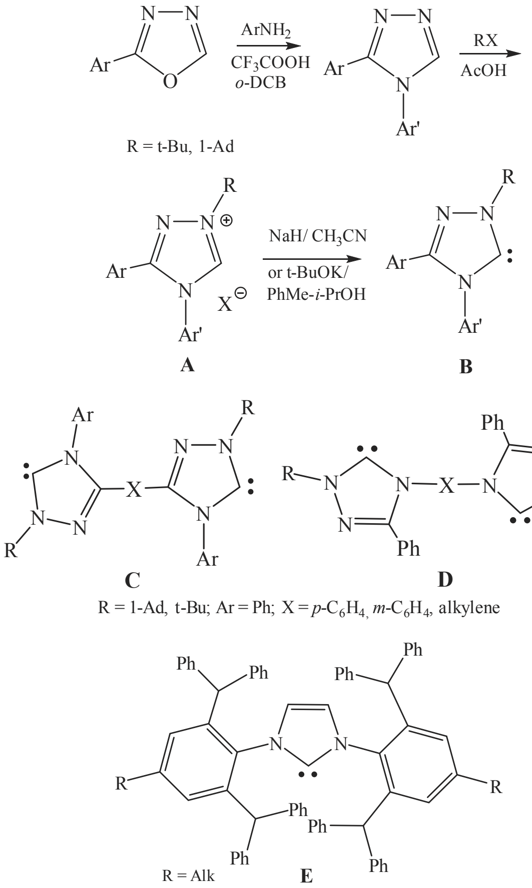
Like their simpler counterparts, the stable heteroaromatic carbenes undergo reactions of inclusion into polar bonds NH, OH, and SH [8, 9] forming carbenoid azolines in which the carbon atom is functionally secured. The authors of [10] have showed that also, the heterocyclic carbenes enter into reactions of inclusion into the C—H bond of acetonitrile (see 1B, Scheme 1). In contrast to triphenylimidazole-1,3,4,5-2-ylidenes and benzimidazole-2-ylidene which react very easily even in the cold, 1,2,4-triazole-5-ylidenes are much less active and form solvates only. These observations have allowed the authors to develop new ways of obtaining the stable carbenes. The first of these methods is deprotonation of sterically shielded 1,3-di(1-adamantyl)benzimidazole salt by sodium hydride in acetonitrile [11—14] (see 1A). Firstly, 2-cyanmethyl derivative is obtained (1B); thereafter, having been heated in vacuum, it readily forms a stable carbene (1C).



Scheme 1

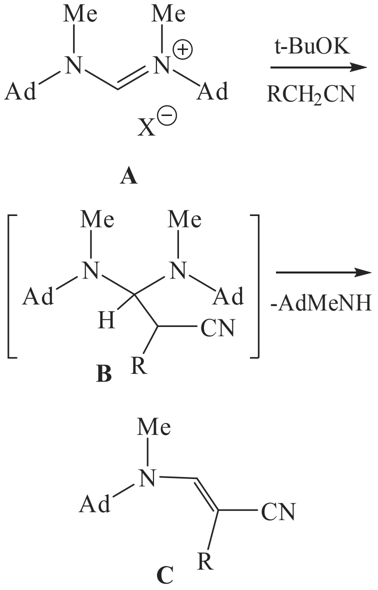
The second way is to deprotonate in the cold 1,2,4-triazole salts (2A) by sodium hydride in acetonitrile, which enables obtaining very pure derivatives of 1,2,4-triazole series (2B) [15], not only the monocarbenes, but also the biscarbenes, including those of conjugated type 2C, D (Scheme 2) [16—18]. Heating the carbenes (2B) with acetonitrile results in the formation of products of carbene inclusion into the C—H bond of acetonitrile [15].

In both cases, for the successful synthesis of individual compounds, the carbene center was protected by acetonitrile (due to the formation of decomposable product of inclusion) or by solvent solvation. An alternative way to protect the carbene center has been implemented during deprotonation of 1,2,4-triazole salts by potassium *tert*-butoxide in toluene mixed with isopropanol or other alcohols. The latter protects the carbene center by creating alcoxiazolines that easily decompose when carbene is separating. In this way, about 30 individual structures of triazole series carbenes have been obtained. Also, a scheme for the synthesis of these carbenes based on oxadiazoles has been designed (Scheme 2).



Scheme 2

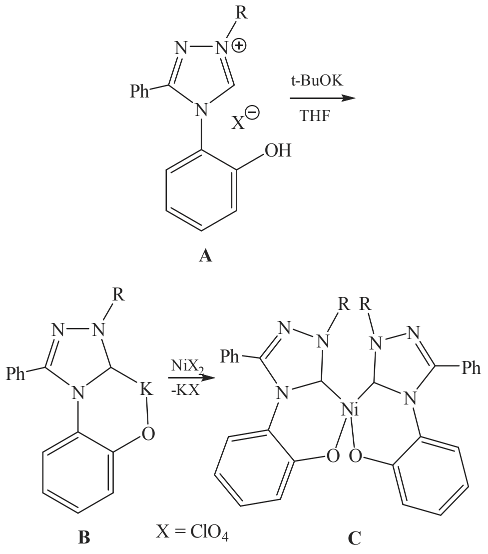
For the diaminocarbene series (3B), the products of inclusion into the C—H bond are unstable and undergo unusual Hoffman carbenoid splitting in non-aqueous medium with the formation of aminoakrylonitriles (3C, Scheme 3) [19] under very gentle conditions.



Scheme 3

To study the properties of carbenes with enhanced steric shielding, stable imidazole-2-ylidenes (2E) with aromatic branched substituents (2,6-dibenzhydryl-4-methyl(ethyl)phenyl — dbmp, dbep) have been synthesized. The properties of these structures are important for the catalysis of organic reactions.

The IPOCC was the first to synthesize a derivative of hypernucleophilic carbenes (4B) by reaction of triazole salt (4A) and potassium *tert*-butoxide in tetrahydrofuran (Scheme 4) [20, 21]. The proton affinity (PA) of 1-*tert*-butyl-3,4-diphenyl-1,2,4-triazole-5-ylidene is theoretically estimated at 265.2 kcal/mole (DFT, B3LYP5, 3-21G, RHF), with that of all nucleophilic carbenes ranging within 247–283 kcal/mole, carbene 4B (286.2 kcal/mole) is major basic and potassium-free anion carbene (from 4B) is hyperbasic (330.5 kcal/mole). Under the action of nickel salts, 4B complex easily exchanges potassium for nickel to form a very stable heteroaromatic complex 4C.



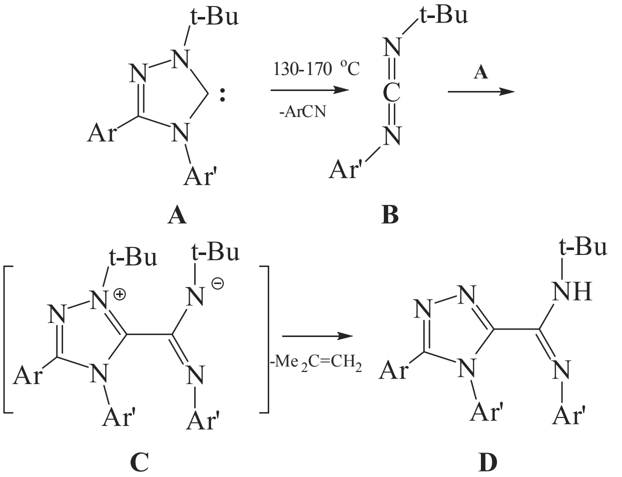
Scheme 4

GENERAL PROPERTIES OF STABLE CARBENES

The total energy of stabilization of hetero-aromatic nuclei without substituents (E_S) for carbenes synthesized is estimated at 92.4 kcal/mole for imidazole-2-ylidene, 100.1 kcal/mole for 1,2,4-triazole-5-ylidene, and at 138.2 kcal/mole for benzimidazole-2-ylidene [22]. The aromatic stabilization energy (R_a) is estimated at 27.5, 30.4, and 21.9 kcal/mole, respectively. Chemical rigidity of these nuclei (5.47, 6.38, and 6.68 eV) ranges within the limits typical for the nucleophilic carbenes. However, depending on the type of structure and substitutes, the properties of these compounds vary widely. For example, in the catalysis of transesterification reactions, benzimidazolylidene (1C) (and imidazole-2-ylidenes close to it) are the most active compound, while 1,2,4-triazole-5-ylidenes (2B—D) and, especially, imidazole-2-ylidenes (2E) with branched aromatic substituents show a significantly less activity.

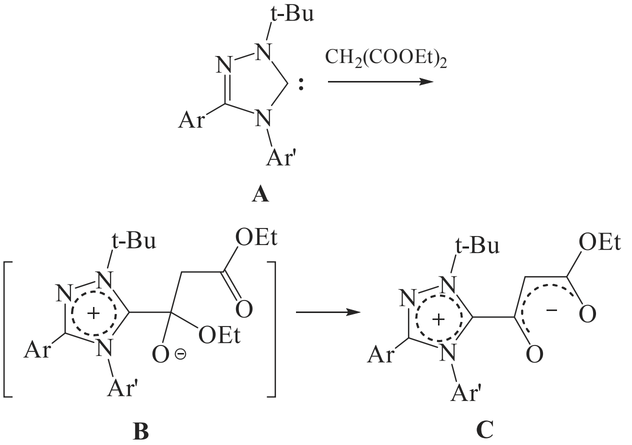
CARBENE TRANSFORMATIONS

Auto-transformations. Unlike for the simple carbenes, for the heteroaromatic carbenes, the rearrangements with proton migration and the formation of olefins are not typical, while the migrations of electrophilic groups from the nitrogen atom to the carbene carbon atom are often reported [23]. 1,3-di(1-adamantyl)imidazole-2-ylidene is thermally stable up to 240 °C [5]. 1,2,4-triazole-5-ylidenes undergo thermolysis with the formation of nitrile and carbodiimides. In the case of 1-*tert*-1,2,4-triazole butyl-substituted-5-ylidenes (5A), there is observed an induced tandem reaction resulting in the formation 5-amidine-1,2,4-triazoles (5D) (Scheme 5) [24, 25].



Scheme 5

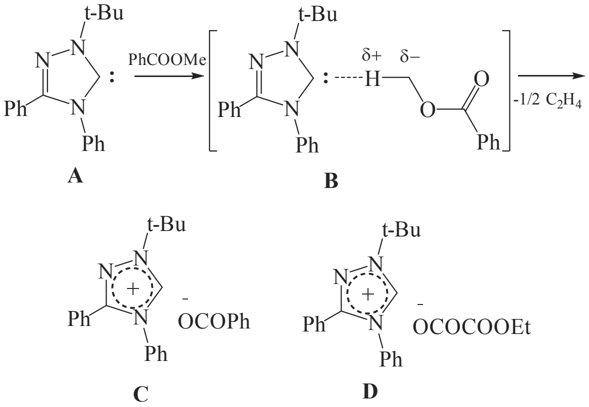
Formation of zwitterionic compounds. Claisen carbene reaction. The heteroaromatic carbenes (6A) can form zwitterionic compounds (6C) when reacting with esters as exemplified by a reaction with malonic ester (Scheme 6) [26].



Scheme 6

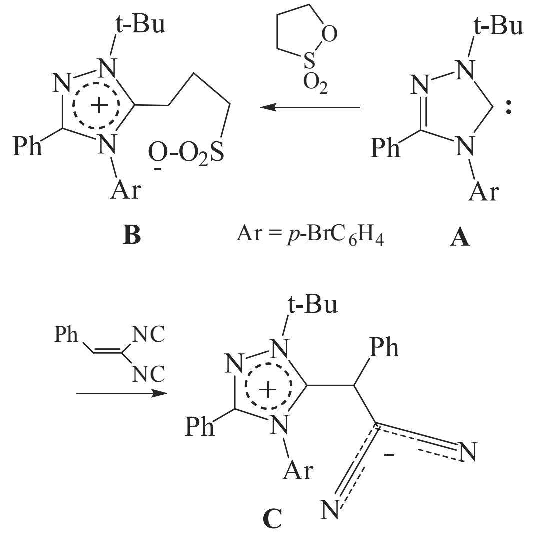
The transformation if the first carbene version of the Claisen reaction.

Reactions with other esters result in deesterification with the formation of salts of respective acids (7C, D) (Scheme 7) [27].



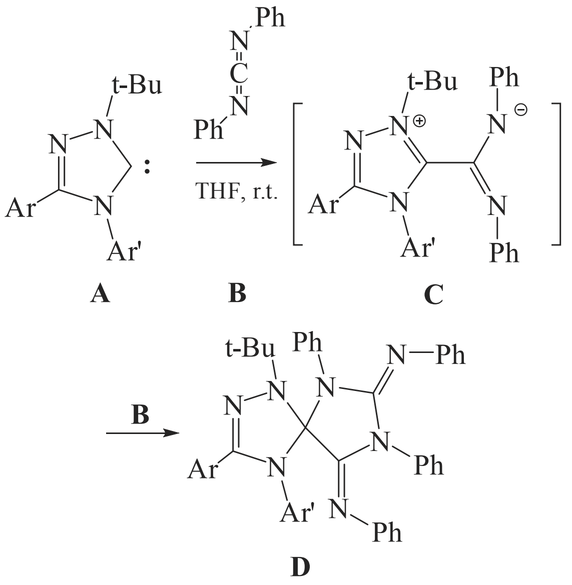
Scheme 7

The reactions with cyclic sulfoesters and electrophiles containing conjugated fragments run towards the formation of zwitterions (8B, C) (Scheme 8) [27].



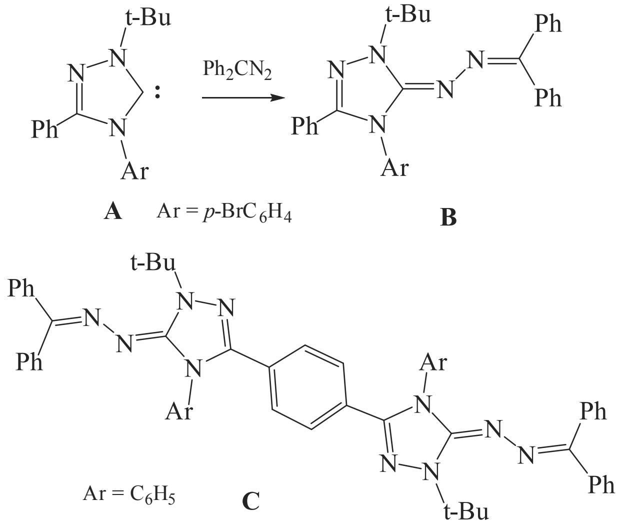
Scheme 8

Addition and cyclization reactions. The addition and cyclization reaction of carbenes with diarylcarbodiimides goes through the zwitterionic (9C) to the spirocyclic compounds (9D) (carbenospirocyclization) (Scheme 9) [23].



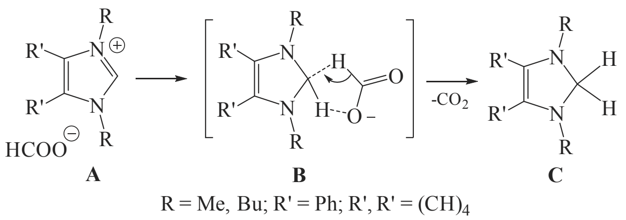
Scheme 9

Nitrene addition of diazocompounds to the carbenes gives conjugated azines (10B, C) and opens up a way to polymeric structures of similar type (Scheme 10) [28].



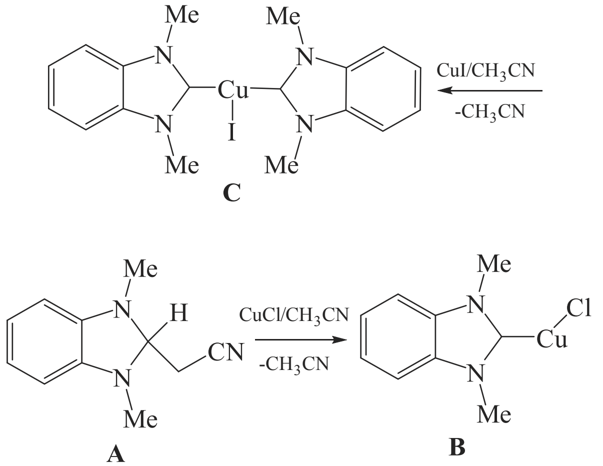
Scheme 10

Carbene version of the Leuckart–Wallach reaction (carbenoid auto-reduction of azolium cations). When heating the formiates of imidazolium and benzimidazolium, the auto-reduction (i.e. intramolecular reduction) takes place with the formation of 2H-azolines (11C) (Scheme 11) [29].



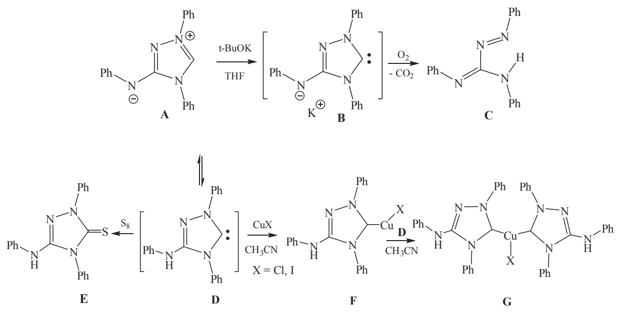
Scheme 11

Carbenoid reactions of 2-cyan-methyl-azolines. The products of inclusion of carbenes into C–H-bond of acetonitrile (2-cyan-methyl-2H-benzimidazolines) are capable of not only generating stable carbenes (see Scheme 1), but also of reacting with salts of transition metals with the formation of carbene complexes (12B, C) (Scheme 12) [28, 30].



Scheme 12

Carbene reactions of mezoionic compounds. Mezoionic 1,4-diphenyl-1,2,4-triazole-3-phenylamide (13A) under the action of potassium *tert*-butoxide forms hyper-nucleophilic carbene (13B) that in the presence of even small quantity of oxygen undergoes oxidation with the formation of azoamidine (13C) (Scheme 13) [27]. While being heated, the compound 13A generates a carbene (13D) that easily reacts with sulfur to form respective thione (13E) and with copper salts to form carbene complexes (13F, G).



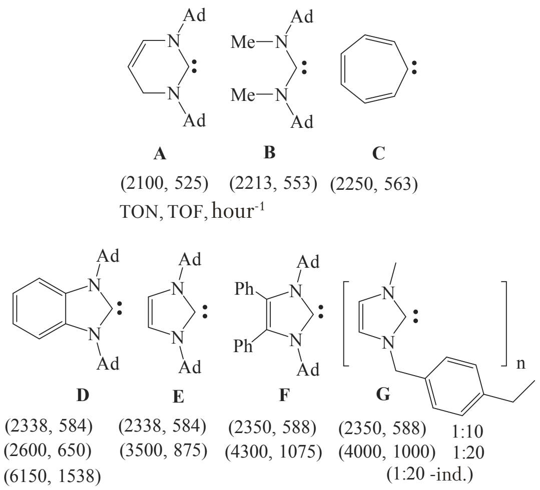
Scheme 13

Hence, it has been established that the following reactions are typical for the heteroaromatic carbenes and can be used for the synthesis: *1)* inclusion into C—H bonds, *2)* auto-induced tandem reactions, *3)* formation of zwitterionic compounds with the esters (the Clausen carbene reaction), *4)* reactions with electrophiles having conjugated fragments, *5)* carbene spirocyclization (formation of spirocyclical compounds) with carbodiimides, *6)* Hofmann carbenoid splitting, *7)* deesterification, and *8)* addition reactions. New carbenoid reactions of reduction, oxidation, and complex formation have been found.

CATALYTIC PROPERTIES OF CARBENES AND THEIR DERIVATIVES

Individual carbenes can catalyze organic reactions, including transesterification and benzoin condensation [31].

Carbene catalysis. For the transesterification of ethyl benzoate in methanol (4 hours, r.t.), the most effective are adamantyl derivatives (14A,B,D—F), cycloheptaylidene (14C), and polymeric carbene (14G) (up to TON 2350, TOF 588 hour^{-1} at a reactant ratio of 1:10 and TON up to 4300, TOF 1075 hour^{-1} at a reactant ratio 1:20) (Scheme 14) [32, 33] (TON is number of catalytic transformation cycles, which is equal to the ratio of the mole number of product to the mole number of catalyst under given conditions and describes the effectiveness of catalyst; TOF is TON per unit of time (usually, 1 hour); describes the productivity of catalyst).

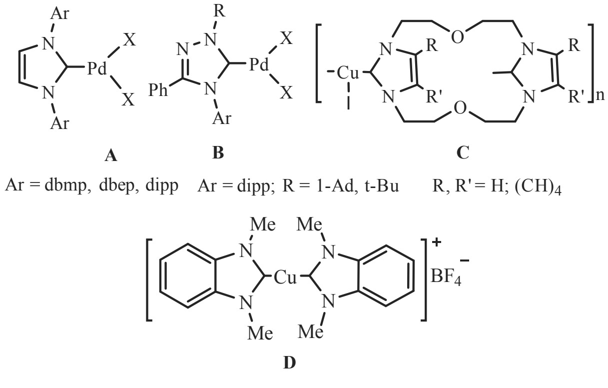


Scheme 14

The individual carbene 14D is more effective (TON 6150, TOF 1538 hour^{-1}) than any kind of *in situ* generated carbenes and shows the highest effectiveness in transesterification reactions. The reaction is used for production of biodiesel.

Carbene 14D is the most effective in benzoin condensation reaction (TON 120) surpassing the well-known Enders carbene (TON 78).

Catalysis by carbene complexes of transition metals. For the haloarene hydrohalogenation that is important for the disposal of persistent organic pollutants (POPs), the most effective are the palladium carbenes complexes with branched aromatic substituents (15A,B), especially 15A (TON up to 318000, TOF 13350 hour^{-1}) (Scheme 15) [34–37]. Effectiveness of 15A (R = dbep) exceeds 10–30 times that of well-known catalysts.



Scheme 15

Complexes 12C, 15C have been established to be the most effective catalysts for the hydrogen transfer reaction (TON up to 50000—85000, TOF up to 20000—32000 hour^{-1}) [30, 38, 39]. As compared with the widely used catalysts, the copper complexes (I) are much more (orders of magnitude more) effective and cheaper.

Catalyst 15D has manifested itself to be more effective than the best known one for the reaction of azide cyclic addition to acetylenes (click-chemistry) (TON 20000, at ambient temperature, versus almost same values, at 50 °C).

CONCLUSIONS

The above examples show prospects for the application of carbonates and carbene transition metal complexes in the industry. The effectiveness of the created catalysts for biofuel synthesis (in five years, Japan plans to switch the whole aviation fleet to seaweed biofuel) and the catalysts for POPs deactivation even today is sufficient for industrial applications. New effective catalysts offer opportunities for the development of «green» chemistry methods aimed at eliminating wastes and improving safety substantially.

It should be noted also that the carbene complexes of transition metals as well as their precursors have antimicrobial and, according to published data, antitumor activity, which is very promising for the healthcare industry, for the search of new drugs [40–44].

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М.І. Коротківх[1], В.Ш. Сабєров[2], Г.Ф. Раєнко[1],
Н.В. Глиняна[1], А.В. Кнішевицький[2], О.П. Швайка[1]
[1] Інститут фізико-органічної хімії і вуглехімії
ім. Л.М. Литвиненка НАН України, Київ
[2] Інститут органічної хімії НАН України, Київ

ХІМІЯ СТАБІЛЬНИХ КАРБЕНІВ ТА «ЗЕЛЕНІ» ТЕХНОЛОГІЇ

Наведено короткий аналіз результатів фундаментальних досліджень з хімії стабільних карбенів та прикладних розробок на їх основі з «зеленої» хімії, що проведені в Інституті фізико-органічної хімії і вуглехімії ім. Л.М. Литвиненка НАН України за останнє десятиліття. Відкрито карбенові версії реакції естерної конденсації Кляйзена з утворенням цвіттеріонних сполук, реакції Лейкарта–Валлаха з автовідновленням карбеноїдних азолієвих солей, розщеплення продуктів вклинення амінокарбенів за Гофманом, індуковану тандемну автотрансформацію 1,2,4-триазол-5-іліденів у 5-амідино-1,2,4-триазоли. Знайдено нові карбенові реакції приєднання, деестерифікації, оксидації та комплексоутворення. Запропоновано ефективні методи одержання стабільних карбенів. та карбеноїдів. Синтезовані нові типи карбенів: бензімідазоліліденu, надстабільні кон'юговані біскарбени та нові типи карбеноїдів. Теоретично передбачено і експериментально доведено існування гіпернуклеофільних карбенів. Показана перспективність використання карбенів та їх похідних (зокрема карбенових комплексів перехідних металів) в каталізі органічних реакцій та пошуку біологічно активних сполук.

Ключові слова: гетероароматичні карбени, синтез, властивості, перетворення, каталіз, біологічна активність, «зелена» хімія.

Н.И. Коротких[1], В.Ш. Саберов[2], Г.Ф. Раенко[1],
Н.В. Глиняная[1], А.В. Книшевицкий[2], О.П. Швайка[1]
[1] Институт физико-органической химии и углехимии
им. Л.М. Литвиненко НАН Украины, Киев
[2] Институт органической химии НАН Украины, Киев

ХИМИЯ СТАБИЛЬНЫХ КАРБЕНОВ И «ЗЕЛЕНЫЕ» ТЕХНОЛОГИИ

Представлен краткий анализ результатов фундаментальных исследований по химии стабильных карбенов и прикладных разработок на их основе в области «зеленой» химии, проводившихся в Институте физико-органической химии и углехимии им. Л.М. Литвиненко НАН Украины за последнее десятилетие. Обнаружены карбеновые версии эфирной конденсации Кляйзена с образованием цвиттерионных соединений, реакции Лейкарта–Валлаха с автовосстановлением карбеноидных азолиевих солей, расщепления по Гофману продуктов внедрения аминокарбенов, индуцированная тандемная автотрансформация 1,2,4-триазол-5-илиденов в 5-амидино-1,2,4-триазолы. Найдены новые карбеновые реакции присоединения, деэтерификации, окисления и комплексообразования. Предложены эффективные методы получения стабильных карбенов и карбеноидов. Синтезированы новые типы карбенов: бензимидазолилидены, сверхстабильные сопряженные бискарбены и новые типы карбеноидов. Теоретически предсказано и экспериментально подтверждено существование гипернуклеофильных карбенов. Показана перспективность использования карбенов и их производных, в частности карбеновых комплексов переходных металлов, в катализе органических реакций и поиске биологически активных соединений.

Ключевые слова: гетероароматические карбены, синтез, свойства, превращения, катализ, биологическая активность, «зеленая» химия.

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