*Chemistry of Heterocyclic Compounds, Vol. 48, No. 1, April, 2012 (Russian Original Vol. 48, No. 1, January, 2012)*

# INTRAMOLECULAR CYCLIZATIONS OF FUNCTIONALIZED DIYNES

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*Examples of intramolecular cyclizations of functionalized diacetylenes are considered in the review. Cyclizations occur with the participation of one of the triple bonds that leads to ethynyl-substituted heterocycles, or of two triple bonds that is used in the synthesis of polycondensed heterocyclic systems and ensembles.*

**Keywords:** benzofuran, benzosilole, benzothiophene, buta-1,3-diyne, indazole, indole, condensed heterocycles, ethynyl-substituted heterocycles, heterocyclic ensembles, biscyclization, intramolecular cyclization,

Intramolecular cyclizations of functional derivatives of acetylene are well known from the middle of the last century. When first mentioned, these reactions were used in the synthesis of benzofuran, indole, and isocoumarin [1-3] derivatives. At the present time, functionalized acetylenic compounds are actively used in the synthesis of carbo- and heterocycles, due to the unique ability of the triple bonds to participate in reactions of electrophilic, nucleophilic, radical addition, cycloaddition, and other processes [4,5]. In the last ten years, a significant number of publications have appeared in which compounds containing a conjugated system of triple bonds have been involved in analogous conversions [6-8]. Earlier, in the review by Maretina and Trofimov published in 2002, the application of diacetylene and its derivatives in the synthesis of heterocycles was considered [9]. The present short review is devoted to intramolecular cyclizations of functionalized diacetylenes and includes work in the period from 2000 to 2011.

In the overwhelming majority of studies the cyclization of diacetylenes has been described proceeding as an addition reaction of a nucleophilic functional group to a triple bond in a neighboring position (Scheme 1). Depending on the reaction conditions and the structure of a substrate, reactions may proceed both with retention of one of the triple bonds and also involving both triple bonds in cyclization. For the activation of diacetylenic compounds, as in the case of monoacetylenic derivatives, two main approaches are used. In the first case, the functional group is activated by the action of bases (I) or using metal complexes (II). In the second case, the triple bond undergoes electrophilic activation, mainly on using metal catalysis (III), or by the action of electrophilic reagents (IV). The first part of the review is devoted to consideration of reactions of this type.

In the second part a few examples are given of intramolecular cyclizations of diacetylenes proceeding as coordinated processes.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 100-111, January, 2012. Original article submitted November 14, 2011.

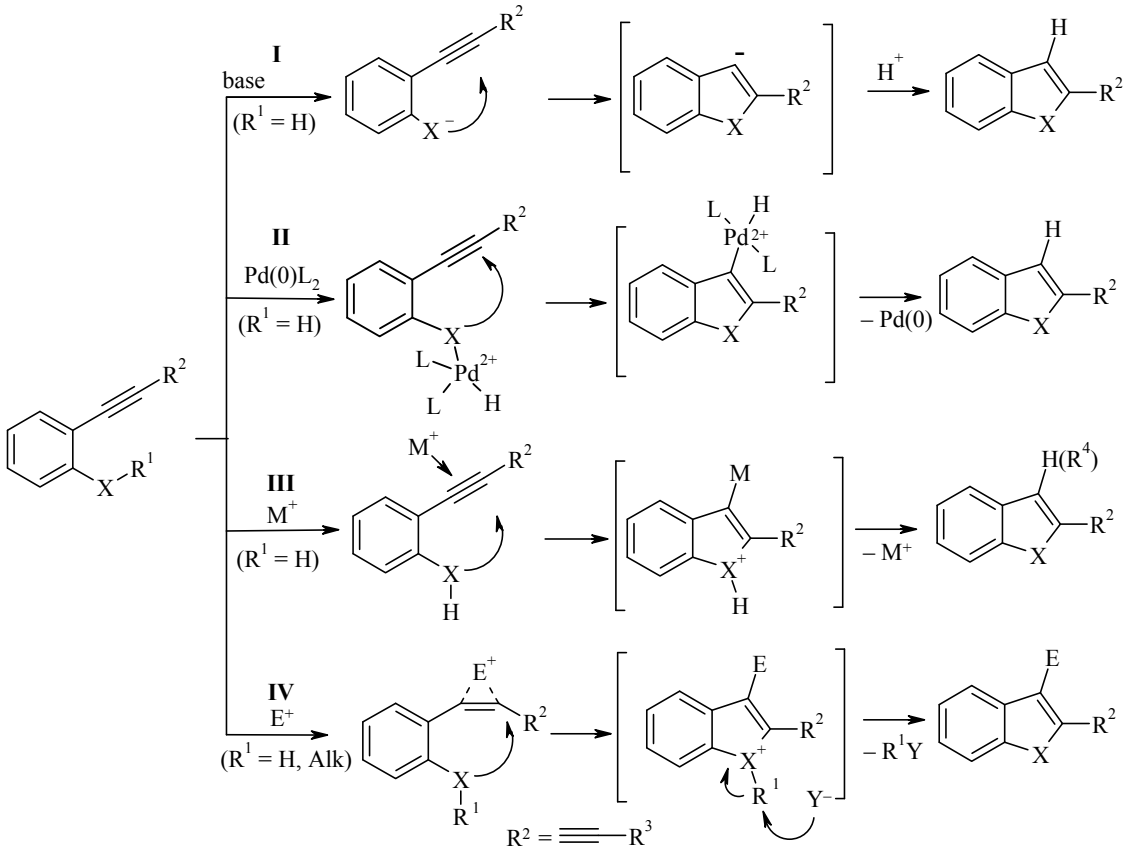
 

## 1. INTRAMOLECULAR ADDITION TO A TRIPLE BOND

All examples of cyclization of functionalized diacetylenes as a result of intramolecular addition to a triple bond occur according to the *endo-dig* type and depending on the nature of the functional group lead to the formation of five- and six-membered heterocycles annelated with the initial aromatic nucleus.

If the cyclization proceeds according to mechanisms I, II, III (Scheme 1) or on electrophilic activation (IV, $E^+ = H^+$) the cyclization products are 2-substituted heterocycles. Introduction of an additional substituent (alkenyl, aryl) into position 3 is possible on electrophilic activation of the triple bond in the case of metal catalysis by complexes of palladium (III, $M^+ = Pd^+$), when the palladium intermediate is active in the formation of a new C–C bond. The cyclization product also obtains an additional substitutent in the case when halogen is used for activation (IV, $E^+ = Hal^+$).

Scheme 1




**I** X = NH, O; **II** X = $NCOCF_3$; **III** $M^+ = Cu^+, Ag^+, Pd^{2+}, Au^{3+}$; X = NH(Alk, Acyl), O, S; $R^4$ = Aryl, Alkenyl;
**IV** $E^+ = H^+, Hal^+$; X = NH(Alk, Acyl), O, S, COO; $Y = Hal^-$, base

In this section, primarily will be considered the reactions in which a C–heteroatom bond and a C–H bond are formed at the heterocyclization stage, and, afterwards, the reactions for which the formation of an additional C–heteroatom or C–C bond also takes place upon forming the heterocyclic ring will be discussed.

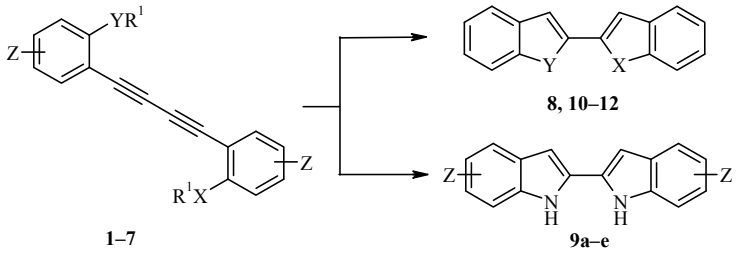
### 1.1. Preparation of 2-Substituted Heterocycles

The most typical functional groups participating in ring closure as a result of addition at a triple bond are amino and hydroxyl groups. These single-type intramolecular cyclization reactions proceed with involvement of one or two triple bonds and lead to the formation of 2-ethynylindoles (or benzofurans) or bisindoles (or benzofurans), respectively.

One of the first methods of obtaining the 2,2'-bisindole **8**, which is a key fragment of synthetic analogs of natural antibiotics, antiseptics, and antitumor preparations, was the cyclization of symmetrical buta-1,3-diyne **1** (Scheme 2) under the action of sodium ethylate upon boiling in ethanol [10]. Later bisindole **8** was obtained on cyclizing the diacetylene **2** by the action of potassium hydride [11], but the use of catalysis by $Au^{3+}$ salts enabled cyclization to be effected at room temperature in aqueous ethanol, in accordance with the principles of "green chemistry" [12].

Metal catalysis with salts of monovalent copper to activate the triple bond in buta-1,3-diynes **3, 4a-d** on boiling in DMF has been applied to obtain a series of bisindoles **9a-e** (Scheme 2). The synthesized compounds were used as key substrates for obtaining supramolecular structures, which are applied in development of sensitive sensors and receptors of various anions [13-19].

Scheme 2




**1, 2, 5–7** Z = H; **3, 9e** Z = 4,4'-(N=N–Ar)$_2$-6,6'-I$_2$; **4a, 9a** Z = 4,4',5,5'-(OBn)$_4$; **4b, 9b** Z = 4,4'-(CO$_2$R)$_2$-6,6'-I$_2$; **4c, 9c** Z = 4,4'-(*t*-Bu)$_2$-6,6'-(NO$_2$)$_2$; **4d, 9d** Z = 4,4'-(*t*-Bu)$_2$-6,6'-I$_2$

| Diyne | X | Y | R$^1$ | Reaction product (yield, %) | Reaction conditions |
|---|---|---|---|---|---|
| **1** | NH | NH | $CO_2Et$ | **8** (86) | NaOEt, EtOH, Δ [10] |
| **2** | NH | NH | H | **8** (70) | KH, NMP, 80 °C [11]<br>$NaAuCl_4 \cdot 2H_2O$, EtOH, 23°C [12] |
| **3, 4a–d** | NH | NH | H | **9a–e** (50–93) | CuI, DMF, Δ [13–19] |
| **5** | O | O | Me | **10** (58) | *p*-TsOH, EtOH, 160°C, MW [20] |
| **6** | S | O | Me | **11** (76) | *p*-TsOH, EtOH, 160°C, MW [20] |
| **7** | $SiMe_2$ | $SiMe_2$ | H | **12** (35) | LiNaph, THF, 23°C [21, 22] |

Cyclization of the symmetrical bis(2-methoxyphenyl)buta-1,3-diyne (**5**) with the formation of bisbenzofuran (**10**) proceeded upon electrophilic activation of the triple bond with *p*-toluenesulfonic acid [20]. Under the same conditions the unsymmetrical 2-[(2-methoxyphenyl)buta-1,3-diynyl]thioanisole (**6**) was subject to cyclization with the formation of the unsymmetrical product **11**, containing furan and thiophene rings [20].

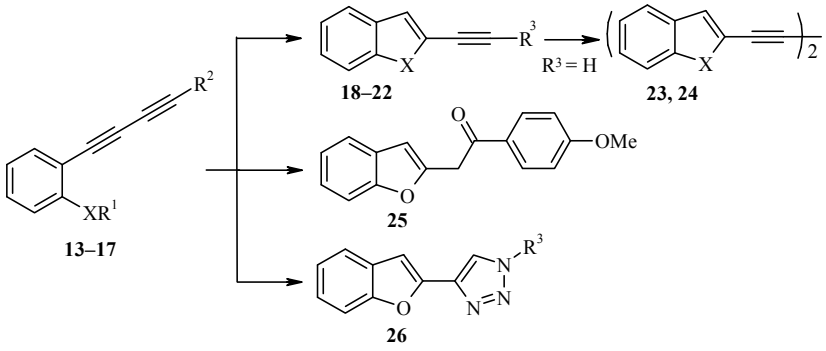
In the case of the biscyclization of silane **7**, authors suppose that in the first stage a two-electron transfer is effected at each triple bond by the action of lithium naphthalide, and subsequent closure of the ring occurs upon nucleophilic attack of the silicon atom by the carbanion, that gives the corresponding bisbenzosilole **12** [21,22].

Cyclizations occurring with the participation of one of the triple bonds leads to the formation of ethynyl-substituted heterocycles (Scheme 3). Under conditions of base catalysis at room temperature compounds **13** and **14** are converted into the corresponding 2-ethynylindoles **18** and **19** [23, 24]. These same authors showed that cyclization of *O*-TBDMS-*o*-(buta-1,3-diynyl)phenol **15** occurred with the formation of 2-ethynylbenzofurans **24, 21**, and **20** under the action of copper(II) salts, on treatment of a solution of compound **15** with tetrabutylammonium fluoride (TBAF), and under cross-linking conditions, respectively. Thus, on attempting to obtain *o*-(4-arylbuta-1,3-diynyl)phenols by cross-linking compound **15** with iodoarenes using a Pd–Ag catalytic system in the presence of potassium carbonate in methanol, removal occurred not only of TMS, but also of the TBDMS protecting group and the phenols formed *in situ* were cyclized into 2-ethynyl-benzofurans **20** [23].

There are examples of monocyclization in which a triple bond not participating in cyclization is subject to conversion in the course of the reaction.

When using copper salts in a catalytic system in cases of a TMS-substituted triple bond, desilylation was observed with dimerization of the initially formed 2-ethynyl-indole **19** or benzofuran **21**, as a result of which compounds **23, 24** were isolated (Scheme 3) [24].

Scheme 3




| Diyne | X | $R^1$ | $R^2$ | Reaction product (yield, %) | $R^3$ | Conditions |
|---|---|---|---|---|---|---|
| **13** | NH | H | Ar | **18** (50–68) | Ar | KH, NMP, 23°C [23] |
| **14** | NH | H | TMS | **19** (68) | H | KH, NMP, 23°C [24] |
| **14** | NH | H | TMS | **23** (50) | — | CuCl, DMF, 70°C [24] |
| **15** | O | TBDMS | TMS | **24** (82) | — | $Cu(OAc)_2$, DMF, 70°C [24] |
| **15** | O | TBDMS | TMS | **20** (40–85) | Ar, Het, Vinyl | Pd–Ag, $K_2CO_3$, MeOH $R^3Hal$, DMF, 40°C [23] |
| **15** | O | TBDMS | TMS | **21** (70) | H | TBAF, DMF, 40°C [24] |
| **16** | O | Me | 2-Naphth | **22** (28) | 2-Naphth | *p*-TsOH, EtOH, 160°C, MW [20] |
| **17** | O | Me | 4-$MeOC_6H_4$ | **25** (94) | — | *p*-TsOH, EtOH, 160°C, MW [20] |
| **15** | O | TBDMS | TMS | **26** (56-72) | Alk, Ar | CuI, TBAF, base, $R^3N_3$ [25] |

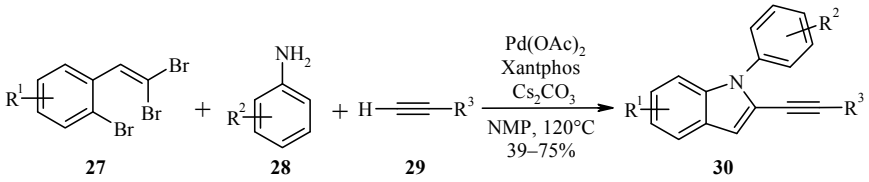
On activating the triple bond of compound **17** with *p*-TsOH the presence of the donor 4-methoxyphenyl substituent leads to hydration of the triple bond with the formation of 2-phenacylbenzofuran **25**, while in the reaction of substrate **16**, having a naphthyl substituent, the reaction product **22** retains the triple bond (Scheme 3) [20].

An interesting example should be mentioned of a simultaneous occurrence of two different cyclizations of the silyl ester of *o*-(buta-1,4-diynyl)phenol **15** using CuI as catalyst in the presence of TBAF and alkyl- or arylazides. Under these conditions the formation of ethynylbenzofuran **21** occurred which interacted *in situ* with the organic azides, giving click reaction products, i.e. 2-(1,2,3-triazol-4-yl)benzofurans **26** [25] (Scheme 3).

The synthesis of *N*-aryl-2-arylethynylindoles **30** (Scheme 4) was carried out in [26] in the presence of palladium complexes as a result of the three-component reaction of substituted *o*-bromo(2,2-dibromo-vinyl)benzenes **27**, anilines **28**, and terminal acetylenes **29**.

One of the mechanisms proposed by the authors was the formation of *o*-bromophenyldiacetylene and a subsequent Buchwald-Hartwig reaction, leading to an aniline, which is cyclized into the final indole by the action of $Pd(OAc)_2$.

Scheme 4

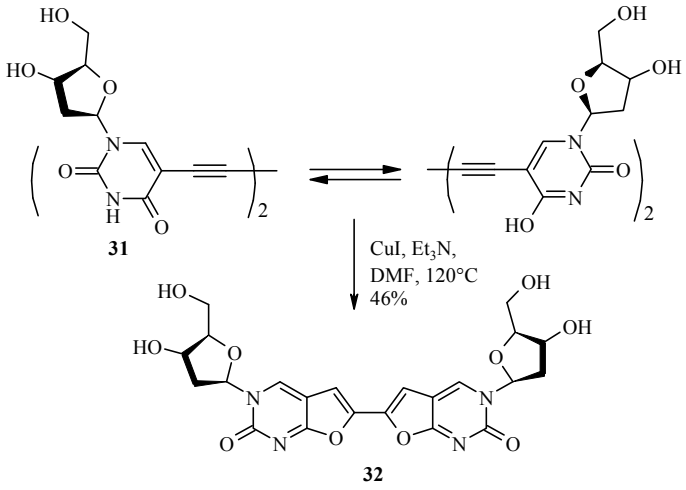



**27** **28** **29** **30**

$R^1$ = H, F, Me; $R^2$ = H, F, Me, OMe, $NO_2$; $R^3$ = Alk, Ar, Het

Among the reactions involving functionalized diacetylenes it is possible to single out the cyclizations describing the assembly of symmetrical polyheterocyclic structures. The synthesis of substituted furopyrimidine **32**, a model compound for the study of biochemical processes, was accomplished starting from buta-1,3-diyne **31** in the presence of a copper iodide and a base (Scheme 5) [27].

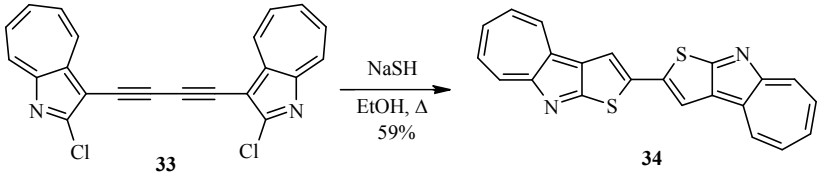
Scheme 5




**31** **32**

Reaction proceeding as a tandem process, i.e. a nucleophilic substitution of chlorine by a thiol group with subsequent closure of the thiophene ring, was described in [28] as a method of obtaining bithieno-azaazulenes **34** (Scheme 6).

Scheme 6

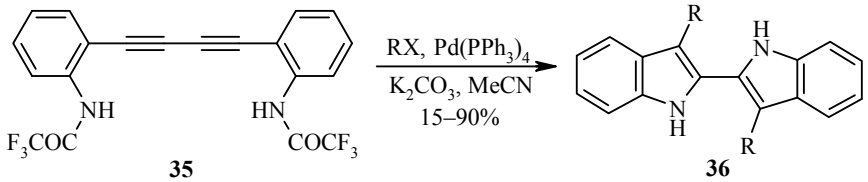



**33** **34**

## 1.2. Cyclizations with Introduction of Additional Substituents

Electrophilic activation of the triple bond with $Pd(PPh_3)_4$ on cyclizing 1,4-[*o*-(trifluoroacetyl-amino)phenyl]butadiyne (**35**) in the presence of aryl halides or aryl-/vinyltriflates was used to obtain 3,3'-di-substituted bisindoles **36** (Scheme 7) [29]. In the first stage of the reaction the occurrence is possible of competing processes forming σ-complexes as a result of the oxidative addition of Pd(0) to the N–H bond of the starting compound **35** or the X–R bond of triflates/iodides. In the first case, cyclization occurs by mechanism II (Scheme 1) and leads to unsubstituted bisindoles [29]. In the second case, the resulting σ-complex of palladium activates the triple bond (route III, Scheme 1) and, after cyclization, reductive elimination of the palladium intermediate formed gives bisindoles **36**, containing substituents in the third position.

Scheme 7



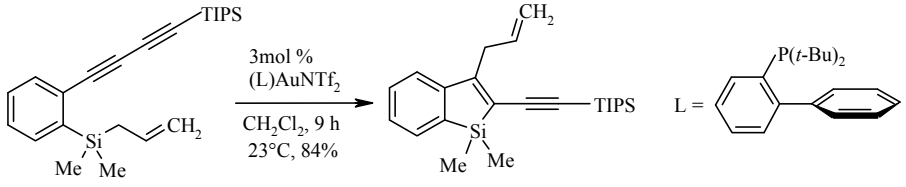

**35** **36**

X = I, R = Ph, 4-$MeO_2CC_6H_4$, 3-$MeO_2CC_6H_4$, 4-$ClC_6H_4$, 4-$MeC_6H_4$, 2,4-$Me_2C_6H_3$, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$;
X = Br, R = 4-$MeCOC_6H_4$, X = OTf, R = 4-$MeC_6H_4$, 1-Naphth, cyclohex-1-en-1-yl

In the case of vinyl triflates and aryl iodides/triflates with a withdrawing substituent in the aromatic ring, only 3,3'-disubstituted bisindoles **36** were isolated from the reaction. In the case of a donating substituent, the reaction proceeds nonselectively, and the formation was observed of a mixture of 3-mono- and 3,3'-disubstituted bisindoles.

Another example of a reaction of this type is the cyclization of allyldimethyl-[2-(buta-1,3-diynyl)-phenyl]silanes **37** under the action of complexes of gold(I) [30], proposed as a method of synthesis of benzosiloles, which are promising compounds for the development of new photo materials. In the presence of gold(I) complexes an intramolecular *trans* allylsilylation of the triple bond occurred in compounds **37**, leading to 2-substituted 3-allyl-1-silaindenes **38** (Scheme 8). The optimum catalyst for this reaction proved to be gold(I) bistriflimide, containing the 2-di-*tert*-butylphosphinobiphenyl ligand.

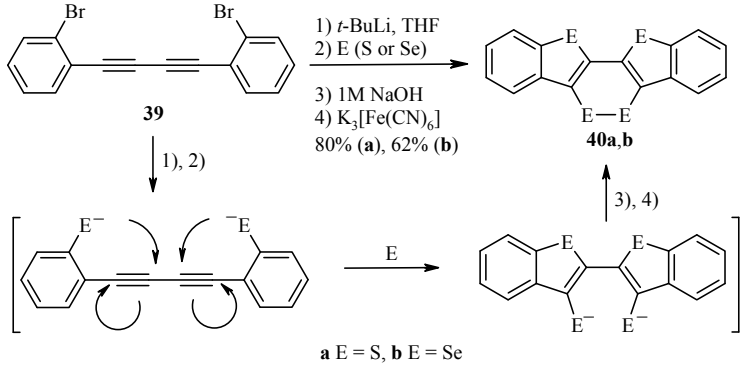
Scheme 8




**37** **38**

One further interesting example of the use of buta-1,3-diynes in a one-pot synthesis of polyannelated thiophene- **40a** and selenopheneheterocenes **40b** was described in [31] (Scheme 9). The introduction of sulfur or selenium atoms into position 3 of the resulting heterocycles occurred *in situ* at the cyclization stage involving the dianionic intermediate formed.

Scheme 9



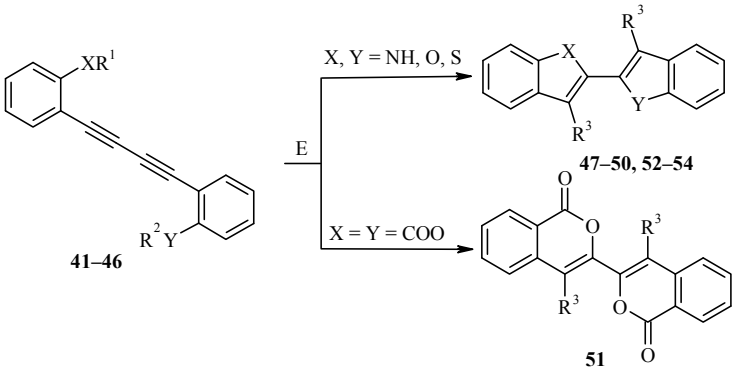

**39** **40a**,**b**

**a** E = S, **b** E = Se

Reactions of electrophilic cyclization of functionalized acetylenes [4], in which the formation of a new C–halogen bond occurs simultaneously with the formation of a heterocyclic ring, are extremely important from the point of view of the possibility of further heterocycle modification with the help of the wide range of cross-coupling reactions. Examples of similar cyclizations have been published recently also for conjugated diacetylenes.

The use of iodine [32], and also bis(pyridine)iodonium tetrafluoroborate [33] and bis(collidine)-iodonium hexafluorophosphate [34] proved to be extremely effective in the synthesis of iodine-substituted unsymmetrical **47** and symmetrical **48-50** bis-heterocyclic compounds (Scheme 10). In the case of the synthesis of bi(4-iodoisocoumarin) (**51**), the cyclization of diester **46** proceeded under the action of a stronger electrophilic reagent, iodine monochloride [35]. Furthermore, bis(3-bromobenzofuran) **53**, -benzothiophene **54**, and also dibromo-substituted 2-(benzothiophen-2-yl)benzofuran **52** were obtained using a mild and effective electrophilic reagent, *N*-methylpyrrolidin-2-one hydrotribromide (MPHT) [36].

Scheme 10

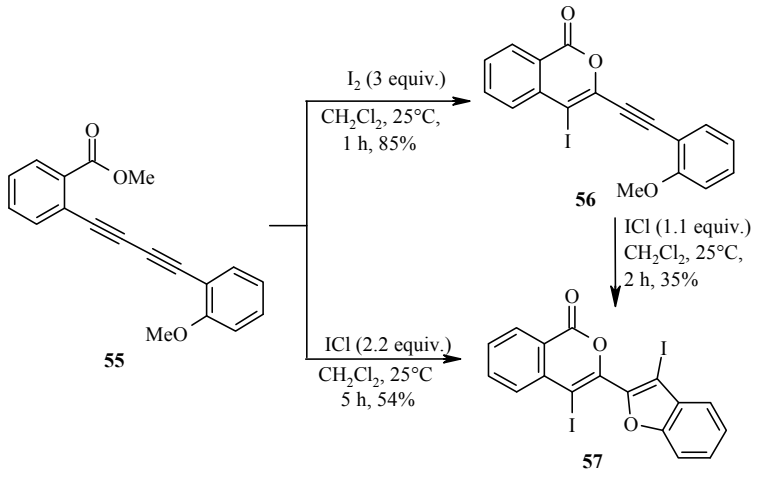



| Diyne | X | Y | $R^1$ | $R^2$ | E (equiv.) | $R^3$ | Reaction product (yield, %) | Reference |
|---|---|---|---|---|---|---|---|---|
| **41** | O | S | Me | Me | $I_2$ (4.0) | I | **47** (94) | [32] |
| **42** | O | O | Me | Me | $I_2$ (4.0) | I | **48** (76) | [32] |
| **43** | S | S | Me | Me | $I_2$ (4.0) | I | **49** (98) | [32] |
| **44** | NH | NH | Boc | Boc | $IPy_2BF_4$ (2.0) | I | **50** (63) | [33] |
| **45** | O | O | EE | EE | $I(coll)_2PF_6$ (4.0) | I | **48** (51) | [34] |
| **46** | COO | COO | Me | Me | ICl (2.4) | I | **51** (90) | [35] |
| **41** | O | S | Me | Me | MPHT (4.2) | Br | **52** (99) | [36] |
| **42** | O | O | Me | Me | MPHT (4.2) | Br | **53** (96) | [36] |
| **43** | S | S | Me | Me | MPHT (4.2) | Br | **54** (97) | [36] |

The electrophilic cyclization of functional derivatives of diacetylene, affecting only one triple bond, is a special case. It enables the preparation of heterocycles containing an ethynyl fragment and a halogen atom on neighboring carbon atoms. The possibility of such a reaction was demonstrated for the first time recently for methyl *o*-(*o*-methoxyphenylbuta-1,3-diynyl)benzoate (**55**), the cyclization of which under the action of iodine proceeded with the formation of 3-ethynyl-4-iodoisochromene **56** (Scheme 11) [32].

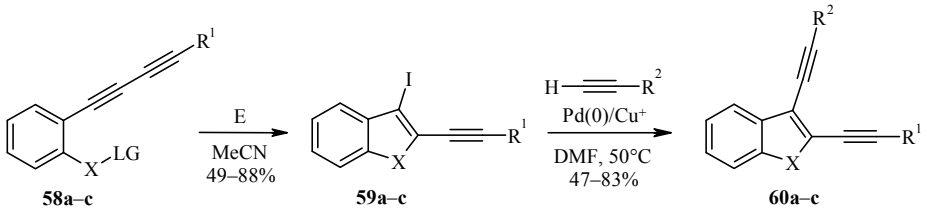
The methoxy group in reactions of this type displays lower reactivity in comparison with methoxycarbonyl group [37] and its participation in cyclization requires the use of ICl. In this case, benzofurylisochromene **57** was obtained [32]. The possibility of carrying out monocyclization was also demonstrated by the example of obtaining 3-bromo-2-(4-methoxyphenylethynyl)benzofuran under the action of MPHT [36].

Scheme 11




In [38], the electrophilic cyclization of diacetylene derivatives was proposed as the key stage in the synthesis of the enediyne systems **60a-c** which, when condensed with benzofuran, benzothiophene, and indole (Scheme 12), are of interest as substrates in the Bergman cyclization [39].

Scheme 12



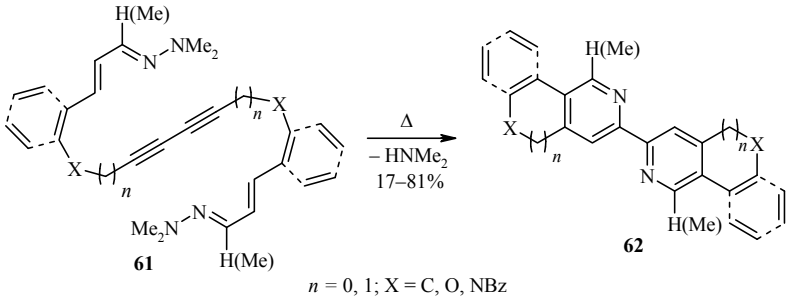

$R^2$ = Alk, Ar, TMS, $(CH_2)_3OH$
**a** X = O, LG = Bn, $R^1$ = Ph, E = ICl (1.5 equiv.); **b** X = NMe, LG = Me, $R^1$ = Alk, Ar, E = $I_2$ (1 equiv.)
**c** X = S, LG = Me, $R^1$ = Ar, Alk, $(CH_2)_2OH$, E = $I_2$ (1 equiv.)

It was shown that the reactivity of *o*-buta-1,3-diynyl derivatives of phenol **58a**, aniline **58b**, and thiophenol **58c** in relation to iodine increases in the series in agreement with the nucleophilicity of the heteroatom of the functional group. To obtain 2-(phenylethynyl)-3-iodobenzofuran (**59a**) the stronger electrophilic reagent ICl was necessary to use.

## 2. COORDINATED CYCLIZATIONS OF FUNCTIONALIZED DIYNES

The prepararion of six-membered heterocycles through the hetero-Diels-Alder reaction with azadienes is a general approach in organic synthesis [40]. In [41], the authors have used the intramolecular Diels-Alder cyclization of bis(azadiene)buta-1,3-diynes **61** to construct bipyridines **62**, annelated with various cyclic systems (Scheme 13). As a result of a double intramolecular [2+4] cycloaddition bipyridines were obtained annelated with five- and six-membered rings and heterocycles of various kind.

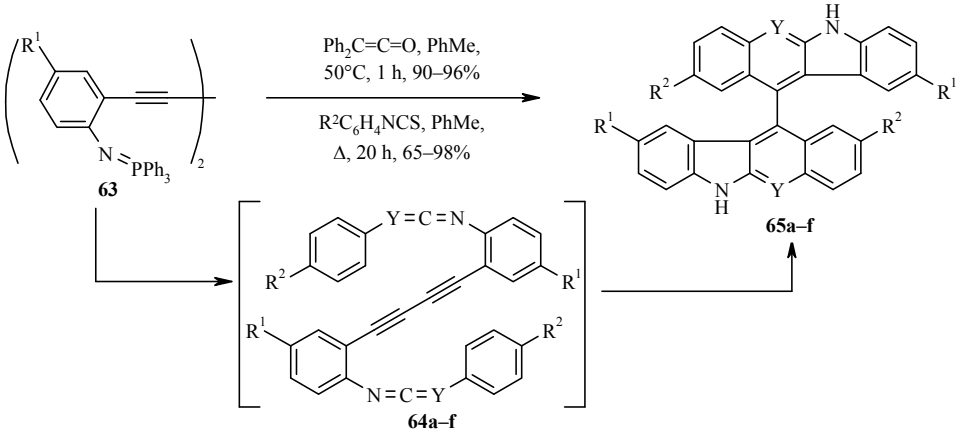
Scheme 13




*n* = 0, 1; X = C, O, NBz

The interaction of diphenyldiacetylenes **63**, containing a phosphazene group in the *ortho* position, with diphenylketene or arylisothiocyanates, and cyclization of the bisketeneimines **64a,b** or biscarbodiimides **64c-f** resulting *in situ,* leads to the corresponding bisbenzocarbazoles **65a,b** and bisquinindolines **65c-f** (Scheme 14). This example is unique since in the course of the reaction polyannelated polyheterocyclic compounds are formed, which were isolated as racemic mixture of two enantiomers in a 1:1 ratio. The chiral structure was confirmed by data of X-ray structural analysis [42].

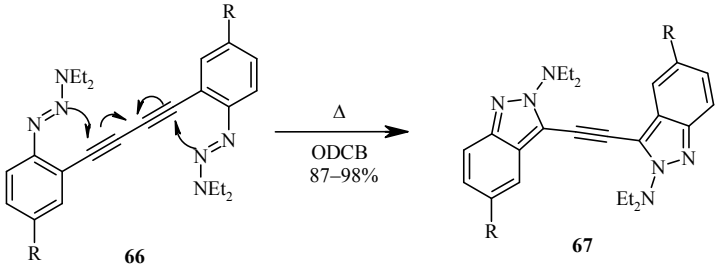
Scheme 14




**a** Y = CPh, $R^1 = R^2 = H$; **b** Y = CPh, $R^1$ = Me, $R^2$ = H; **c** Y = N, $R^1$ = H, $R^2$ = Me; **d** Y = N, $R^1$ = H, $R^2$ = OMe; **e** Y = N, $R^1 = R^2$ = Me; **f** Y = N, $R^1$ = Me, $R^2$ = OMe

Herges and coworkers studied thermal cyclization of diacetylenic derivatives of aryltriazenes **66** in various solvents (ethanol, toluene, *o*-dichlorobenzene (ODCB)). In the case of the symmetrical bistriazene derivatives of butadiyne, bisisoindazolyl-acetylenes **67** were obtained (Scheme 15) [43].

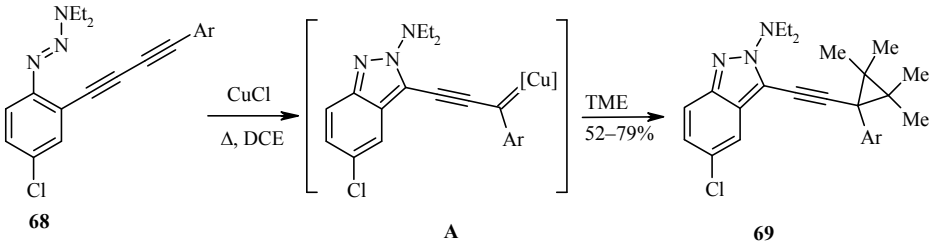
Scheme 15




R = H, *t*-Bu, Cl, $NO_2$, CN, OMe

The cyclization of *o*-(buta-1,3-diynyl)aryltriazenes **68** in the presence of CuCl led to ethynylindazoles **69**, containing a cyclopropyl fragment, formed as a result of [2+1] cycloaddition of 2,3-dimethyl-2-butene (TME) to carbenoid **A** [44] (Scheme 16).

Scheme 16

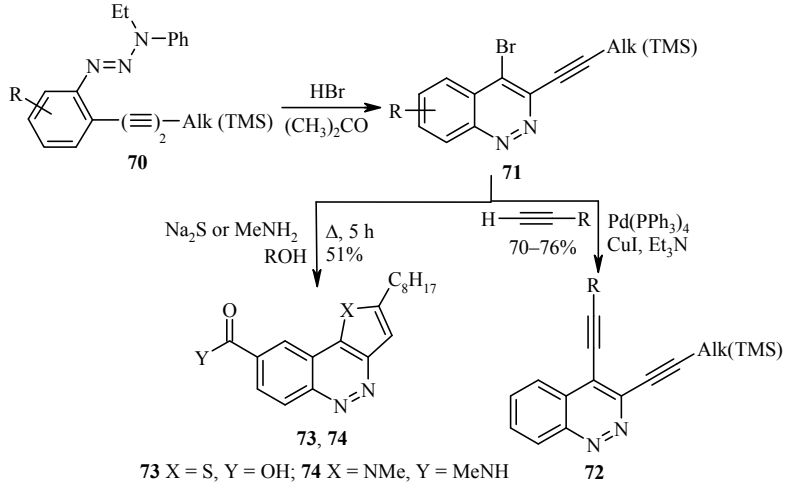



On the basis of the experimental data and data of quantum-chemical calculations the authors concluded that the cyclization is catalyzed by electrophilic activation of the triple bond by $Cu^+$ ions remote from the triazene group.

These transformations are a few examples of *exo* cyclization in a series of functionalized diacetylenes. The transition state in the described processes is called "concerted" [43], since in its formation two triple bonds of the initial triazene are involved, from which one new triple bond is formed in the reaction product.

The cyclization of *o*-(buta-1,3-diynyl)arenediazonium salts (Richter reaction), generated upon decomposing *o*-(buta-1,3-diynyl)aryltriaz-1-enes **70** by the action of HBr [45], has been proposed as a method of synthesizing 4-bromo-3-ethynylcinnolines (Scheme 17).

Scheme 17




Although in previous studies the mechanism of the Richter reaction has been considered to be the result of diazonium ion addition at the triple bond [46], the probable mechanism of this reaction may be electrocyclization. The obtained compounds were used in the synthesis of cinnolines condensed with thiophene **73** and pyrrole **74** rings, and also in obtaining enediyne systems **72** [45, 47].

The use of functionalized diacetylenes in cyclizations affords symmetrical and unsymmetrical polyheterocyclic systems in one step. Cyclizations occurring with the participation of only one triple bond may be used as an alternative approach to ethynyl-substituted heterocycles. Syntheses of heterocyclic systems based on the cyclization of diacetylenes using electrophilic reagents or catalysis by complexes of transition metals in

the presence of additional reagents, or intramolecular fragments able to interact with intermediates, are the most promising among the reactions considered.

The work was carried out with the financial support of St. Petersburg State University (grant No. 12.38.14.2011).

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