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REVIEW

Organometallic Tetrazole Derivatives: Preparation and Application to Organic Synthesis

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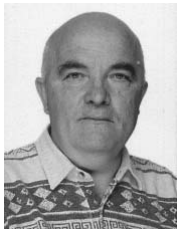
Abstract—The data are integrated and systematized on preparation procedures and application to the organic synthesis of organometallic tetrazole derivatives, including 5-metallated tetrazoles and tetrazoles with a metal-carbon bond in a substituent, and also organotin tetrazoles.

Sergey Voitekhovich was born in 1974 in Polotsk, Vitebsk oblast (Belarus Republic). In 1996 he graduated from Belarussian State University, in 2002 he became Candidate of Sciences. He is Senior Researcher in the Laboratory of Condensed Matter of the Research Institute of Physicochemical Problems at Belorussian State University.

Area of scientific interest: organic synthesis, synthesis and characteristics of tetrazole derivatives.



Pavel Gaponik was born in 1941 in Gortol' village, Brest oblast (Belarus Republic). In 1965 he graduated from Belorussian State University. Candidate of Chemical Sciences since 1970, Doctor of Chemical Sciences since 2001. He is Principal Researcher in the Research Institute of Physicochemical Problems at Belarussian State University.

Area of scientific interest: fundamental and applied problems of tetrazole chemistry, including polymers and metal complexes; regioselective synthesis in the tetrazole chemistry.

Grigorii Koldobskii was born in Leningrad in 1933. In 1956 he graduated from the Leningrad State Technological Institute. He sustained the Thesis of Candidate of Chemical Sciences in 1963, and the Thesis of Doctor of Chemical Sciences in 1974. Professor of the Saint-Petersburg State Technological Institute (Technical University). He is the author of over 350 scientific publications. He was awarded a medal of Karlov University (Czechia).

Area of scientific interest: acid and phase-transfer catalysis of organic reactions, preparation methods and physicochemical characteristics of polynitrogen heterocyclic compounds.

1. INTRODUCTION

In the recent 15–20 years the interest to tetazole and its derivatives has been constantly growing due first of all to a great success achieved in preparation of a number of highly efficient drugs based on tetrazole [1–5]. Various types of tetrazoles are also used as trigger explosives, components of mixed propellants, gas-generating compositions [6, 7]. They also play exceptional part in the synthetic chemistry for preparation of compounds belonging to various classes [8, 9]. The achievements in the tetrazole chemistry originate also from the growing availability of these compounds due to the significant advances in the synthesis where the key role belongs now to the organometallic derivatives of tetrazole. However the data on organometallic tetrazoles are not yet systematized. Only in a review on C-lithiated azoles were collected the publications up to 1995 also on the corresponding tetrazole compounds [10].

The present review is the first attempt to integrate and systematize the data on the preparation procedures and application to the organic synthesis of organometallic tetrazole derivatives, in particular, 5-metallated tetrazoles and tetrazolium salts, and also of tetrazoles containing a metal-carbon bond in a substituent. Furthermore, N-organotin tetrazoles are considered that play an important role in the preparative tetrazole chemistry.

2. 5-METALLATED TETRAZOLES

Two fundamentally different approaches underlie the syntheses of 5-metallated tetrazoles: either the metallation

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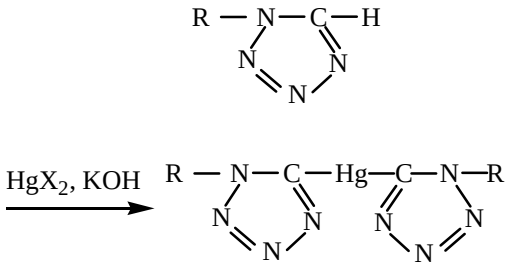
of tetrazoles or the cycloaddition of coordinated azides to isonitriles.

The first approach is sufficiently general since it affords both metal derivatives of 1- and 2-monosubstituted tetrazoles and of the salts of 1,3- and 2,3-disubstituted tetrazoliums. However up till now only mercury(II) salts and organolithium compounds were studies as metallation agents in these reactions.

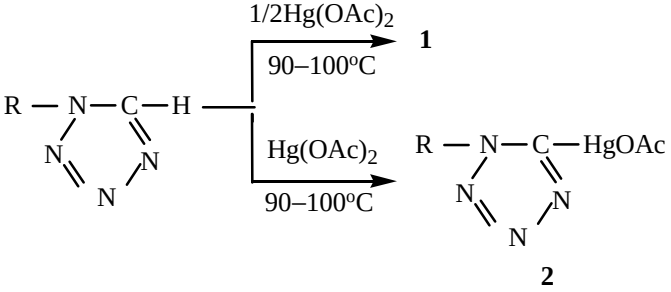
Bis (5-tetrazolyl)mercury derivatives **1** were pepared from 1-monosubstituted tetrazoles and mercury(II) salts in the presence of potassium hydroxide in the lower alcohols (methanol, 2-propanol) at room temperature [11, 12].



1

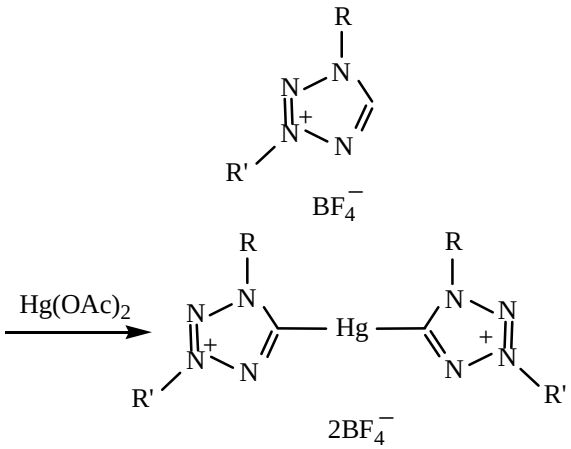
X = Br, OAc; **1**, R = Me (80%), *t*-Bu (80%), All (75%), Ph (85%), Vin.

Compounds **1** (R = Me, Ph) were obtained in fairly good yields (85–95%) by treating appropriate tetrazoles with a system mercury(II) bromide–lithium bromide–sodium hydroxide in aqueous DMF or DMSO [11, 13]. Under the above conditions the mercuration occurred yielding only symmetric mercury derivatives. In a neutral (water) and acid (acetic acid) environment the mercuration of 1-monosubstituted tetrazoles proceeded under more stringent conditions (at boiling), and depending on the reagents ratio bis- or monotetrazolyl mercury derivatives **1** and **2** were obtained [11].



1, R = Me (85%), Ph (60%); **2**, R = Me (90%), Ph (75%).

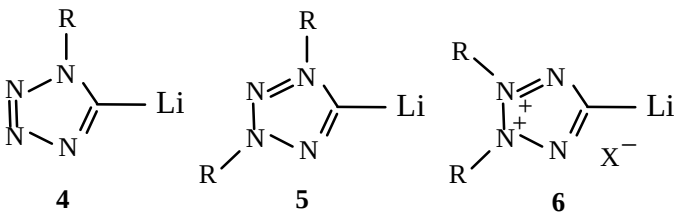
The attempts to perform mercuration of 2-monosubstituted tetrazoles under similar conditions were unsuccessful [11, 14] apparently because of lower CH-acidity of these tetrazoles compared to the 1-monosubstituted derivatives [14–17]. A mecuration of 1,3-diaryltetrazolium salts was described to occur at their heating with mercury(II) acetate in DMSO affording bis(tetrazolio)mercury(II) salts [18]. The structure of salts **3** was confirmed by the data of ^{13}C [18] and ^{119}Hg [19] NMR.



3

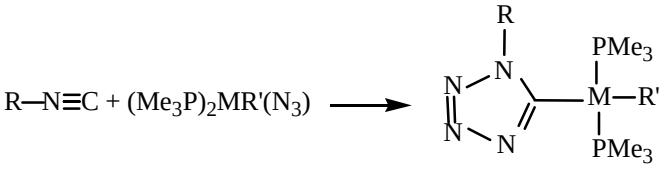
3, R = R' = Ph (82%); R = *p*-MeC_6H_4, R' = Ph (76%); R = Ph, R' = *p*-$MeOC_6H_4$ (56%).

5-Lithiated tetrazoles were prepared by treating with alkyllitium or lithium hexamethyldisilazane N-monosubstituted tetrazoles or tetrazolium salts at low temperature (from –98 to –60°C). The process is commonly carried out in THF, more seldom in ethyl ethter, and sometimes in the presence of *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA). In this way series of 5-lithio-1-R-tetrazoles **4** (R = Me [10], Bz [20, 21], 4-$MeOC_6H_4CH_2$ [21], $BzOCH_2$ [22]), 5-lithio-2-R-tetrazoles **5** (R = $Me_3SiCH_2CH_2OCH_2$ [23], $BzOCH_2$ [24], azabicycloalkyl [25]), and 5-lithio-2,3-diaryltetrazolium salts **6** [26, 27] were prepared. In view of the high reactivity these compounds were not isolated as individual substances but were applied to further reactions in solution.



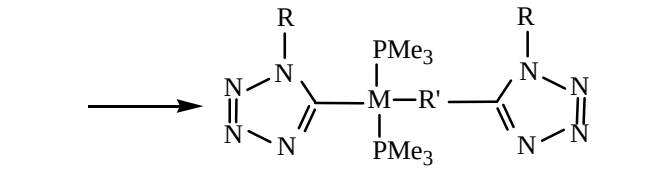
4 **5** **6**

The second procedure of 5-metallated tetrazoles synthesis consists in the cycloaddition of coordinated azides to isonitriles [28]. The reaction is commonly carried out in organic solvent medium at room temperature to afford depending on the structure of the initial complex azide either mono-, bis-, or polytetrazolyl derivatives. Recently this method was used to prepare the corresponding platino- and palladiotetrazoles **7** and **8** [29–33], and also bimetallic tetrazoles **9** [34].



7

7, M = Pd, R = t-Bu, R' = Me (49%); R = C_6H_{11}, R' = Me (56%); R = 2,6-$Me_2C_6H_3$, R' = Me (66%) [29]; R = *t*-Bu, R' = Ph (78%); R = C_6H_{11}, R' = Ph (51%) [30]; R = *t*-Bu, R' = PhC≡C (66%); R = t-Bu, R' = MeOC(O)C≡C (86%) [31]; M = Pt, R = t-Bu, R' = Me (54%) [29].



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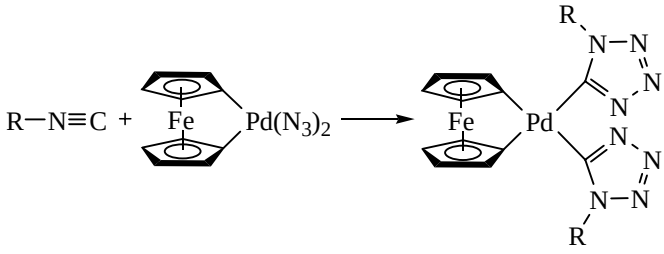
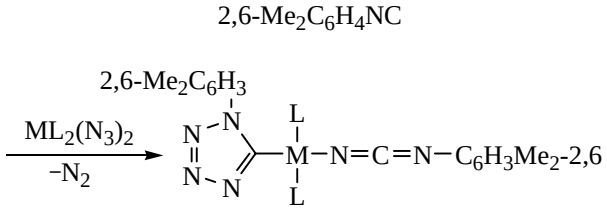


9

8, M = Pd, R = Bu (85%), t-Bu (79%), C_6H_{11} (86%); M = Pt, R = Bu (92%), t-Bu (71%) [32], 2,6-$Me_2C_6H_3$ (76%) [33]; **9**, R = t-Bu (78%), C_6H_{11} (70%) [34].

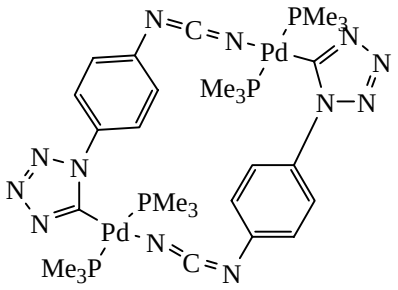
At higher temperature the reaction can yield instead of the expected tetrazoles the corresponding carbodiimide complexes due to the fragmentation of the tetrazole ring with elimination of the molecular nitroigen. Sometimes the reaction can be stopped at the stage of fragmentation of only one from the two tetrazole rings. In this way 5-metal-lated tetrazoles **10** were obtained where the metal is linked to the carbodiimide moiety [31–33].



10

10, M = Pd, L = PMe_3 (79%), PEt_3 (88%), PMe_2Ph (57%), $PMePh_2$ (63%) [32]; M = Ni, L = PMe_3 (43%); M = Pt, L = PMe_3 (54%), PEt_3 (92%) [33].

The similar process involving 1,4-phenylenediisocyanide resulted in formation of a binuclear cyclic complex **11** whose structure was established by the X-ray diffraction analysis [35].



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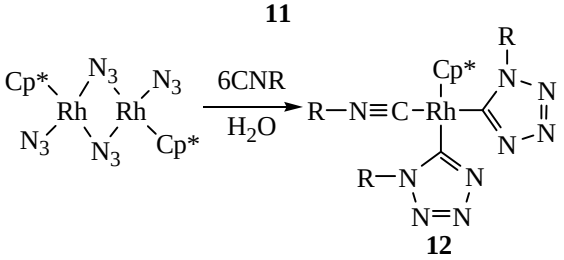
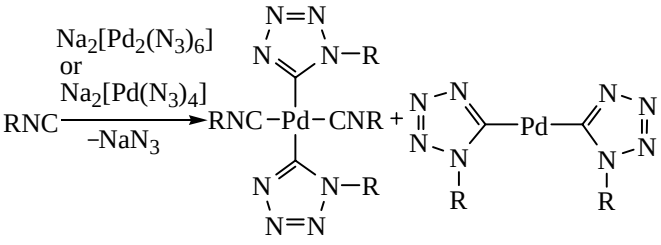


12

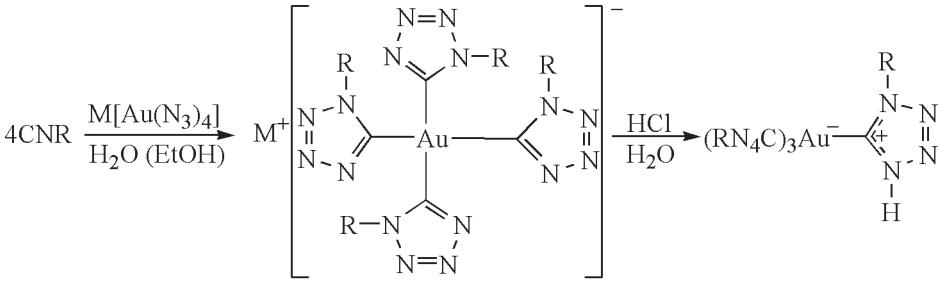
12, R = t-Bu (75%), cyclo-C_6H_{11} (45%), $(CH_2)_3CH_2Cl$ (40%), All (32%), CH_2COONa (10%).

The structure of compound obtained can include as a ligand a molecule of the initial isocyanide. It was found in particular in the synthesis of 5-rhodiotetrazoles **12** and 5-palladiotetrazoles **13** and **14** [36].



13 **14**

R = t-Bu (**13**, 90%), cyclo-C_6H_{11} (**13**, 65%; **14**, 30%), $(CH_2)_3CH_2Cl$ (**13**, 45%; **14**, 45%), All (13, 20%; **14**, 70%).



15

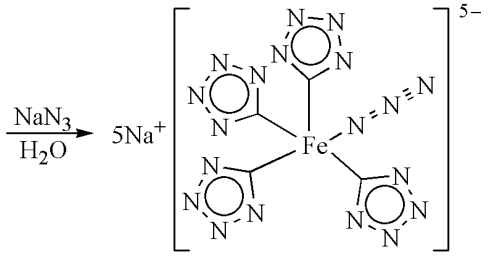
16

15, R = *t*-Bu, M = Na (95%); R = cyclo-C_6H_{11}, M = Li (65%); 16, R = *t*-Bu (95%), cyclo-C_6H_{11} (95%). R = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$, *p*-$Me_3N^+C_6H_4$.

At the same time the reaction of isocyanides with alkali metal tetraazidoaurates generated *in situ* from the corresponding tetrachloroaurates and azides furnished tetrakis(1-R-tetrazol-5-yl)aurates(III) **15** which under treatment with diluted hydrochloric acid yielded compounds with presumable structure **16** where one of the tetrazole rings was protonated [36, 37].

The recent attempt to synthesize a complex $Na_3[Fe(CN)_5(N_2)]$ by reaction of sodium nitroprusside with sodium azide and $NO[SbCl_6]$ resulted in isolation in an 11% yield of a compound that according to spectral data (IR, ^{13}C NMR) was a sodium azidotetrakis-(5-tetrazolato)iron(0) **17** [38]. This conversion is the first example of a synthesis of a stable tetrazole derivative containing a Fe–C^5 bond, and it opens a prospect of preparation of similar compounds from accessible complex ferrocyanides.

$$Na[Fe(CN)_5(NO)](H_2O)_2$$



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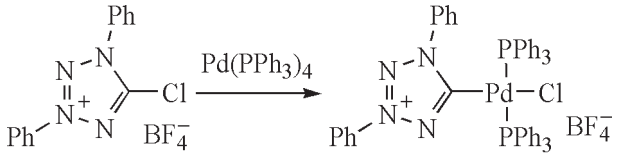
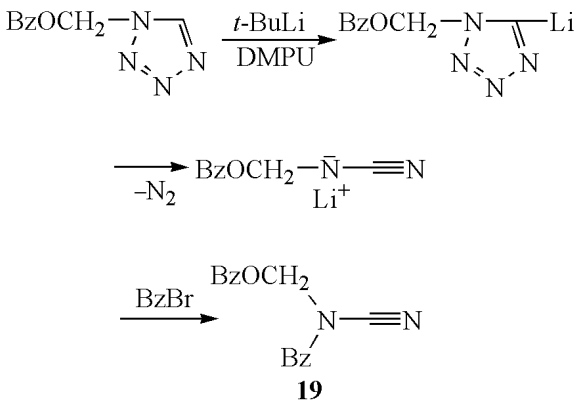
Alongside the replacement of a hydrogen the metal atom can be introduced into the C^5 position of the tetrazole ring by insertion into a C–Cl bond as shows the example of the synthesis of chloro(1,3-diphenyltetrazolio-5-yl)di(triphenylphosphine)palladium tetrafluoroborate (**18**, 85%) from 5-chloro-1,3-diphenyltetrazolium tetrafluoroborate and tetrakis(triphenylphosphine)palladium(0). Analogous synthesis of the corresponding platinum derivative failed [18].



18

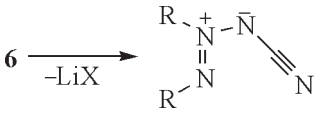
Physicochemical characteristics of 5-metallated tetrazoles are poorly understood. It should be noted however that the properties of the compounds, their stability in particular, essentially depend on the nature of the metal involved. For instance, the mercury compounds **1–3** are relatively stable (decomposition temperature exceeds 140°C) [11, 12, 18] except for bis(1-vinyltetrazol-5-yl)mercury(II) which is highly sensitive to mechanical actions and requires careful handling [12]. 5-Lithiotetrazoles **4–6** are considerably less stable and can decompose even at low temperature. For instance, tetrazole **4** (R = $BzOCH_2$) in ethyl ether and TMEDA decomposes already at –100°C, whereas its isomer **5** (R = $BzOCH_2$) is stable under similar conditions [24]. In the case of 1-R-5-lithiotetrazoles **4** the electron-withdrawing substituents R, like Ph and $BzOCH_2$, decrease the decomposition temperature as compared to compounds with donor substituents (Me, Bz) [24]. The main decomposition path of 1-substituted 5-lithiotetrazoles consists in frag-



19

mentation yielding molecular nitrogen and N-monosubstituted cyanamides. This fragmantaion path was recently confirmed by obtaining N,N-disubstituted cyanamide **19** at successive treatment of 1-benzyloxymethyltetrazole with butyllithium and benzyl bromide at –78°C in THF in the presence of *N*,*N*-dimethyltetrahydropyrimidin-2-one [24].

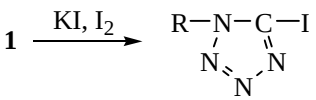
5-Lithio-2,3-diaryltetrazolium salts **6** obtained at –78°C at warming to room temperature suffered the opening of the tetrazole ring to furnish 2,3-diaryl-1-cyanoazimines in 63–85% yields [26, 27].



Bis(1,3-diphenyltetrazolio)mercury underwent opening at treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) giving 1,3-diphenyl-3-cyanotriazene in a 79% yield [18].

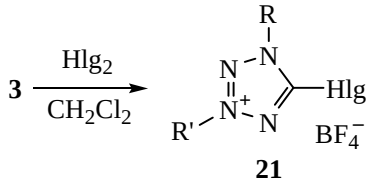
In spite of a large nitrogen content (up to 30%) the gold derivatives **15** and **16** are highly stable up to 210–220°C when they melt with decomposition. However they decomposed under X-ray irradiation which prevented performing their structural analysis [36]. At the same time the other 5-metallated tetrazoles containing rhodium [36], palladium [29, 32], and platinum [32, 33, 36] were successfully subjected to the X-ray diffraction analysis.

The characteristic reaction of 5-metallated tetrazoles is the metal replacement. Among these reactions halodemetallation of tetrazole mercury derivatives is of significant preparative interest: This is the main way of halogen introduction unto the C^5 position of the tetrazole ring. The preparation of 5-iodo-1-R-tetrazoles **20** is conveniently performed applying a halogenating system iodine–potassium iodid in ethanol: The corresponding 5-iodotetrazoles **20** form at room temperature in an yield over 75% [12].



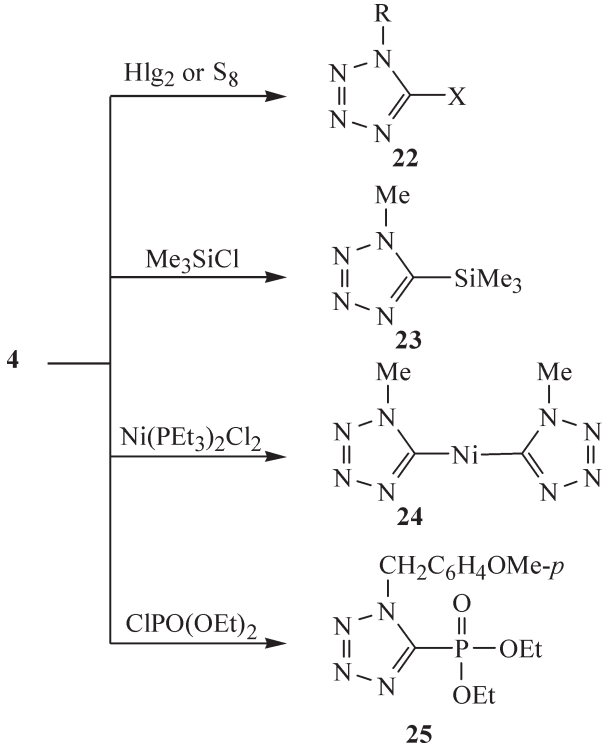
R = *t*-Bu, All, Vin, Ph.

With tetrazolium salts **3** analogous conversions occur cleanly at treating with the halogen in dichloromethane [18].



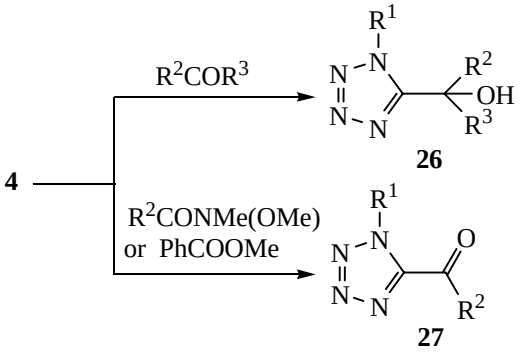
21, R = R' = Ph, Hlg = Cl (59%), Br (54%), I (78%); Hlg = I, R = *p*-MeC_6H_4, R' = Ph (71%), R = Ph, R' = *p*-$MeOC_6H_4$ (62%).

Lithium derivatives **4–6** provide wider synthetic opportunities. Lithiotetrazoles **4** like mercury compounds readily react with halogens affording 5-halo-1-R-tetrazoles **22** {R = Me, X = Br (41%), I (36%) [18]; R = $PhCH_2$, X = Br (82%) [20]; R = *p*-$MeOC_6H_4CH_2$, X = I (54%) [21], $PhCH_2OCH_2$ (84%) [22]}. They are also subjected to reactions resulting in 1,5-disubstituted



26, R^1 = Bz, R^2 = $BzCH_2$, R^3 = H (71%); R^1 = *p*-$MeOC_6H_4CH_2$, R^2 = $BzCH_2$, R^3 = H (73%); R^1 = Bz, R^2 = Ph, R^3 = H (70%); R^1 = p-$MeOC_6H_4CH_2$, R^2 = Ph, R^3 = H (80%); R^1 = Bz, R^2, R^3 = $(CH_2)_6$ (78%); R^1 = *p*-$MeOC_6H_4CH_2$, R^2, R^3 = $(CH_2)_3CH{=}CH$ (93%) [21]; R^1 = $BzOCH_2$, R^2 = Ph, R^3 = H (71%); R^1 = R^2 = $BzOCH_2$, R^3 = H (65%); R^1 = $BzOCH_2$, R^2, R^3 = $(CH_2)_5$ (56%); R^1 = $BzOCH_2$, R^2, R^3 = $(CH_2)_3CH{=}CH$ (60%); R^1 = $BzOCH_2$, R^2 = BocHNCHBz, R^3 = H (27%) [22]; 27, R^1 = *p*-$MeOC_6H_4CH_2$, R^2 = $PhOCH_2$ (52%); Ph (62%) [21]; R^1 = $BzOCH_2$, CBzHNCHBz (65%) [22].

tetrazoles **22** (R = Me, X = S, 67%), **23** (43%), **24** (80%) [18], **25** (68%) [21] containing other heteroatoms in the C^5 position.



26, R^1 = Bz, R^2 = $BzCH_2$, R^3 = H (71%); R^1 = *p*-$MeOC_6H_4CH_2$, R^2 = $BzCH_2$, R^3 = H (73%); R^1 = Bz, R^2 = Ph, R^3 = H (70%); R^1 = p-$MeOC_6H_4CH_2$, R^2 = Ph, R^3 = H (80%); R^1 = Bz, R^2, R^3 = $(CH_2)_6$ (78%); R^1 = *p*-$MeOC_6H_4CH_2$, R^2, R^3 = $(CH_2)_3CH{=}CH$ (93%) [21]; R^1 = $BzOCH_2$, R^2 = Ph, R^3 = H (71%); R^1 = R^2 = $BzOCH_2$, R^3 = H (65%); R^1 = $BzOCH_2$, R^2, R^3 = $(CH_2)_5$ (56%); R^1 = $BzOCH_2$, R^2, R^3 = $(CH_2)_3CH{=}CH$ (60%); R^1 = $BzOCH_2$, R^2 = BocHNCHBz, R^3 = H (27%) [22]; **27**, R^1 = *p*-$MeOC_6H_4CH_2$, R^2 = $PhOCH_2$ (52%); Ph (62%) [21]; R^1 = $BzOCH_2$, CBzHNCHBz (65%) [22].

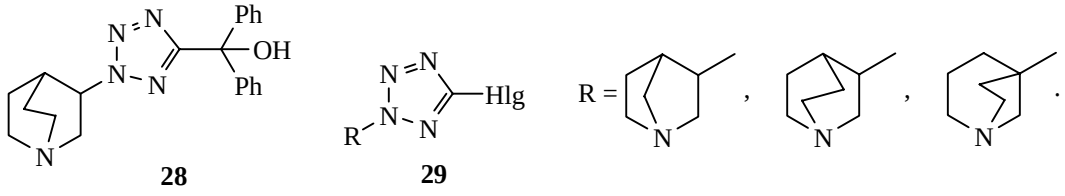
Synthetically significant are the reactions of 5-lithio-1-R-tetrazoles **4** with aldehydes, ketones, esters, and Weinreb amides conveniently leading to 1-substituted 5-hydroxyalkyl- **26** and 5-acyltetrazoles **27** [18, 21, 22].

Also 2-substituted 5-lithiotetrazoles **5** can be successfully brought into these processes as shows the synthesis therefrom of functionally substituted tetrazoles **28** and **29** [25], **30** [23].

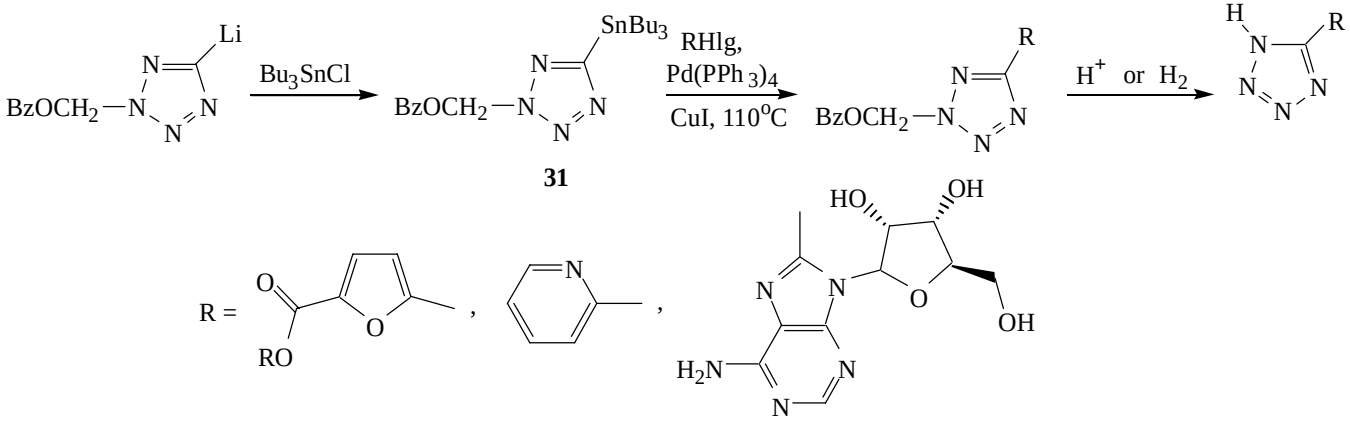
2-Benzyloxymethyl-5-lithiotetrazole reacted with tributyltin chloride to give tin derivative **31**, a convenient reagent for preparation of 5-aryl and 5-hetaryltetrazoles. At boiling of the latter with aryl halides in toluene in the presence of copper(I) iodide and tetrakis(triphenylphosphine)palladium(0) coupling products were obtained in 63–91% where the benzyloxymethyl group could be readily replaced by hydrogen [24].

The treatment of tetrazolium salt 6 with diazonium salts and tosyl azide resulted in formation of 5-arylazo and 5-azido-2,3-diaryltetrazolium salts respectively [27].

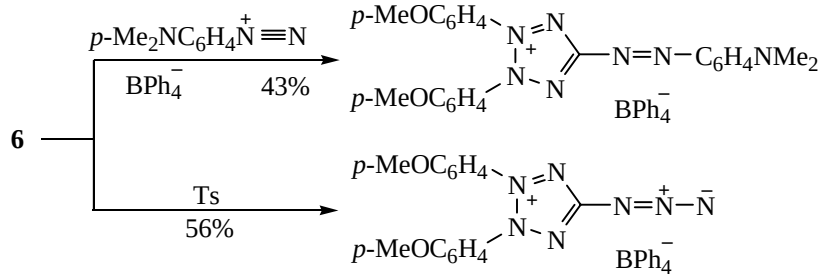
In lithiation of tetrazoles the probable reactions with substituents should be taken into consideration. For instance, reaction of 1-methyltetrazole with *tert*-butyllithium and chlorotrimethylsilane in THF gave rise along-



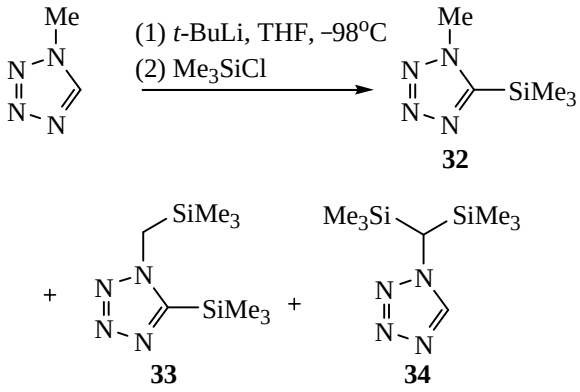
29, Hlg = Cl, Br, I.



R = Ph, 2,6-$Me_2C_6H_3$, 2-$C_6H_5C_6H_4$, 4-$OHCC_6H_4$, 4-$O_2NCC_6H_4$; Hlg = Br, I.



side the expected 1-methyl-5-trimethylsilyltetrazole **32** (43%) also to 1-(1-trimethylsilylmethyl)-5-trimethylsilyltetrazole **33** (16%) and 1,1-bis(trimethylsilyl)tetrazole **34** (13%). The formation of the latter compounds was ascribed to transmetallation of tetrazole **32** [39].



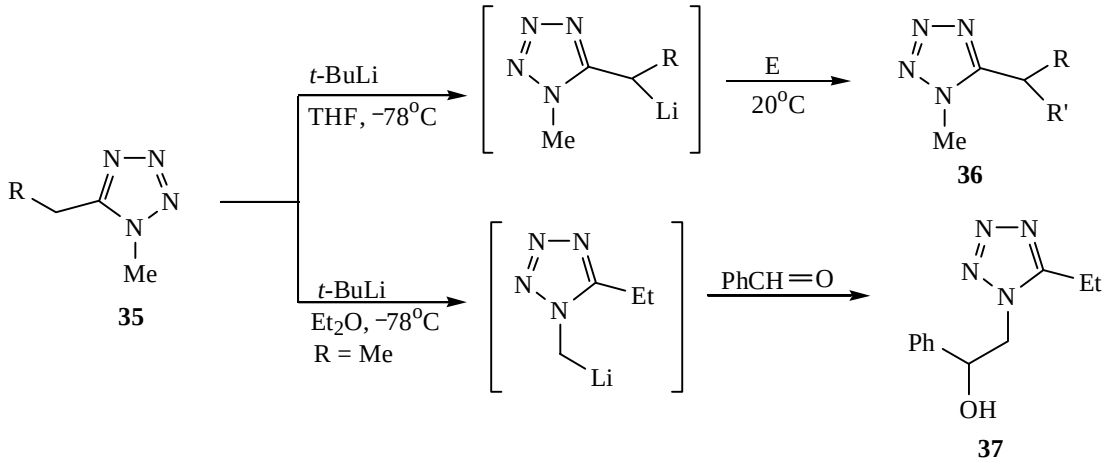
3. TETRAZOLES CONTAINING A METAL–CARBON BOND IN A SUBSTITUENT

3.1. *Tetrazoles with a Metal–Carbon σ-Bond*

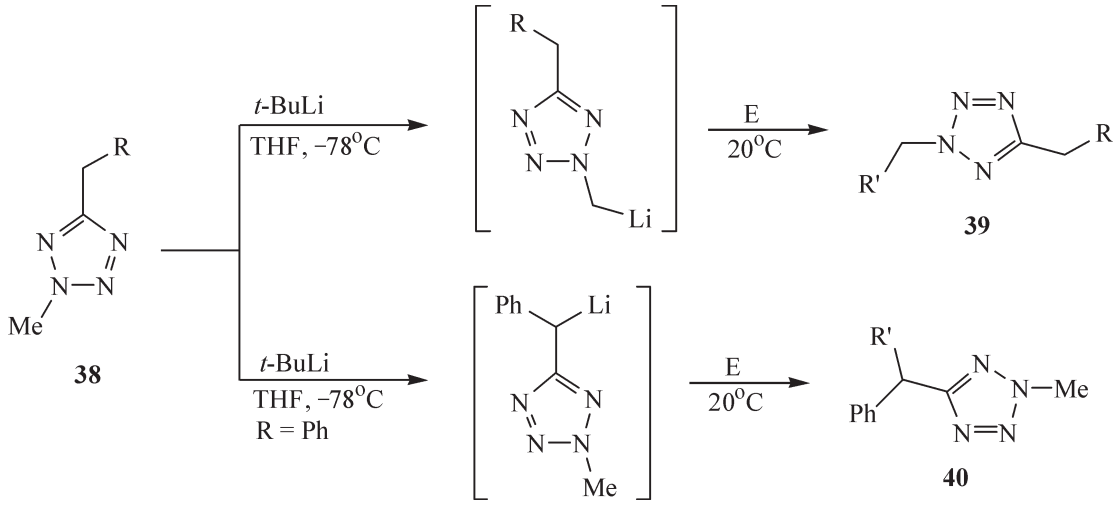
This type compounds are prepared by metallating disubstituted tetrazoles with substituents where α-carbon atoms possess sufficient CH-acidity. Just these atoms suffer lithiation when 1,5- and 2,5-disubstituted tetrazoles are treated with alkyllitium. Lithiotetrazoles thus obtained readily react with electrophilic agents, in particular, with aldehydes, ketones, and alkyl halides. The reactions underlie the functionalization of the C- and N-substituents of the tetrazole ring. The regioselectivity of lithiation and subsequent alkylation of the isomeric 1,5-and 2,5-disubstituted tetrazoles is different all other factors being the same.

1-Methyl-5-alkyltetrazoles **35** are lithiated with butyllithium in THF at the methylene group carbon. The subsequent reaction of the lithium derivative with electrophilic agents (aldehydes, alkyl halides) afforded 1-methyl-5-substituted tetrazoles **36**. The change of the solvent for ethyl ether affected the yield of the product, and in the case of 1-methyl-5-ethyltetrazole the selectivity of the process changes resulting in formation of compound **37** (yield 17%) [40].

2-Methyl-5-alkyltetrazoles **38** under similar conditions underwent lithiation mainly at the N-methyl group. However with the 5-benzyltetrazoles the metallation and



E = MeI, PhCH=O, *t*-BuCH=O, cyclo-$(CH_2)_5$CH=O; **36**, R = R' = Me (16%); R = Me, R' = PhCH(OH) (48%), cyclo-$(CH_2)_5$CH(OH) (54%), *t*-BuCH(OH) (59%); R = OPh, R' = Me (49%), PhCH(OH) (64%), cyclo-$(CH_2)_5$CH(OH) (83%), *t*-BuCH(OH) (90%), Me (72%); R = Ph, R' = PhCH(OH) (44%), cyclo-$(CH_2)_5$CH(OH) (0%), *t*-BuCH(OH) (45%).



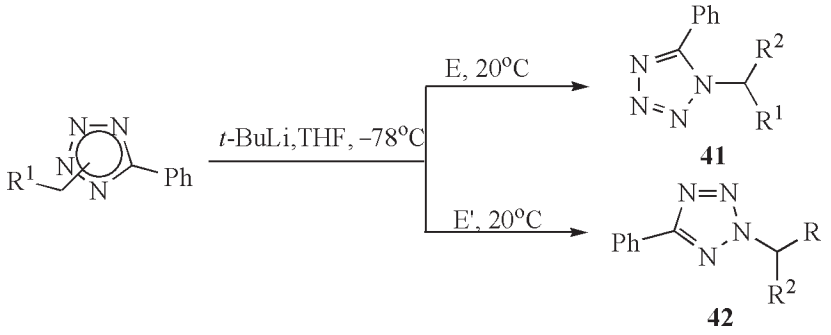
E = MeI, PhCH=O, *t*-BuCH=O, cyclo-$(CH_2)_5$CH=O; **39**, R = R' = Me (48%); R = Me, R' = PhCH(OH) (79%), cyclo-$(CH_2)_5$CH(OH) (51%), *t*-BuCH(OH) (66%); R = OPh, R' = Me (45%), PhCH(OH) (78%), cyclo-$(CH_2)_5$CH(OH) (71%), *t*-BuCH(OH) (95%); **40**, R' = Me (54%), PhCH(OH) (56%), cyclo-$(CH_2)_5$CH(OH) (56%), *t*-BuCH(OH) (44%).

subsequent alkylation occurred at the C-methylene group [40].

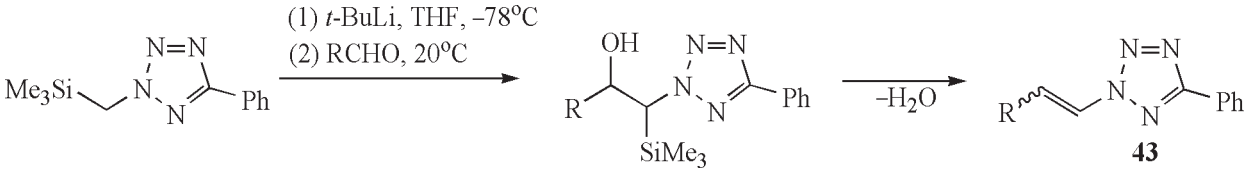
In an attempt to elucidate the cause of observed dissimilar behavior of isomeric tetrazoles **35** and **38** [41] calculations were carried out by MNDO procedure of enthalpy of formation and dipole moments of the reagents, intermediates, and reaction products of metallation under treatment with *tert*-butyllithium followed by methylation with methyl iodide of 1- and 2-methyl-5-ethyltetrazoles **35** and **38** (R = Me). It was revealed that thermodynamics of the processes favors formation of 1,5- and 2,5-diethyltetrazoles whereas due to the kinetic parameters the formation of 1- and 2-methyl-5-(2-propyl)-tetrazoles is more feasible.

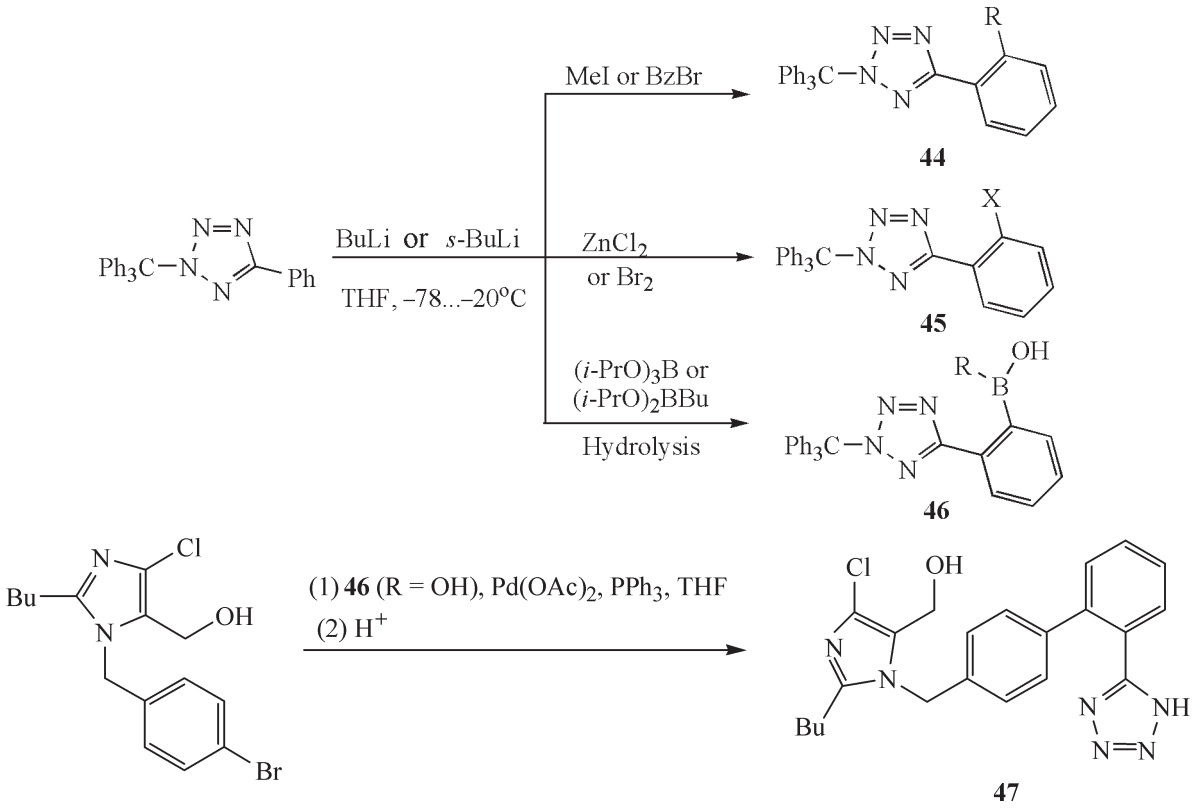
N-Alkyl-5-phenyltetrazoles under analogous conditions underwent substitution at the α-carbon of the alkyl group furnishing N-functionally substituted 5-phenyltetrazoles **41, 42** [42, 43].

The application of 2-trimethylsilylmethyl-5-phenyltetrazole as a substrate in these processes proved to be



E = D_2O, Me_3SiCl, Me_2SO_4, Ar_2CO, ArCHO, ArCN (Ar = 4-MeC_6H_4); E' = Me_3SiCl, CO_2; R^3CHO (R^3 = H, Et, Ph, 4-$MeOC_6H_4$); **41**, R^1 = H, R^2 = D (96%), Me_3Si (96%), Me (90%), CAr_2OH (84%); R^1 = Ar, R^2 = CAr_2OH (95%), CH(OH)Ar (87%), COAr (80%); **42**, R^1 = H, R^2 = Me_3Si (70%), CH_2OH (33%), CH(OH)Et (85%), CH(OH)Ar (77%); R^1 = Me, R^2 = COOH (53%), CH(OH)Ph (98%).



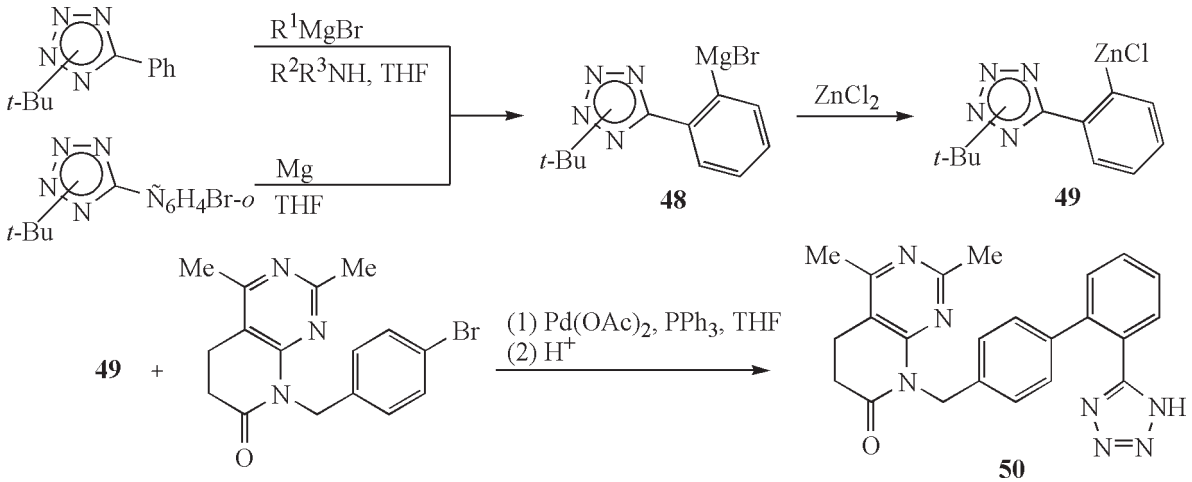


44, R = Me (88%), Bz (42%) [44]; **45**, X = Br, ZnCl [47]; **46**, R = Bu (85%) [45], OH (90%) [46].

a convenient procedure for preparation of 2-(1-alkenyl)-tetrazoles **43** [R = Et (68%), R = *t*-Bu (88%)]. Therewith in the case of a bulky *tert*-butyl substituent R only *E*-isomer of tetrazole **43** formed in a high yield [42, 43].

2-Triphenylmethyl-5-phenyltetrazole was lithiated at the *ortho*-carbon of the phenyl group attached to the tetrazole ring [44–47]. The further transformations of the lithiated tetrazole are important for the synthesis of compounds **45** and **46** which are easily subjected to cross-coupling and which are synthetic precursors of antihypertensive drugs based on 5-(*ortho*-biphenyl)-tetrazoles, in particular, Losartan **47** [46].

N-*tert*-Butyl-5-phenyltetrazole that also lacked hydrogen atoms at the α-carbon of the alkyl group was metallated with Grignard reagents in the presence of diisopropylamine or 2,2,6,6-tetramethylpiperidine to afford a product of the phenyl group *ortho*-metallation **48** [48]. The same compound was prepared from magnesium and



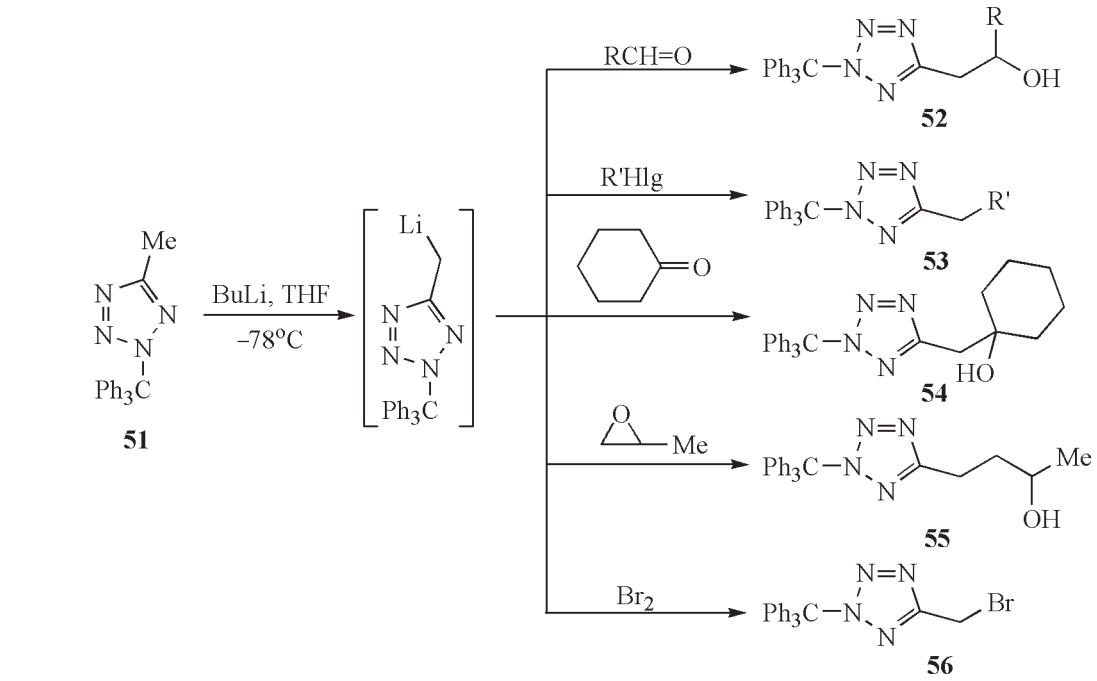
R^1 = Me, Et, Bz; R^2 = R^3 = i-Pr; R^2, R^3 = $CMe_2(CH_2)_3Me_2C$.

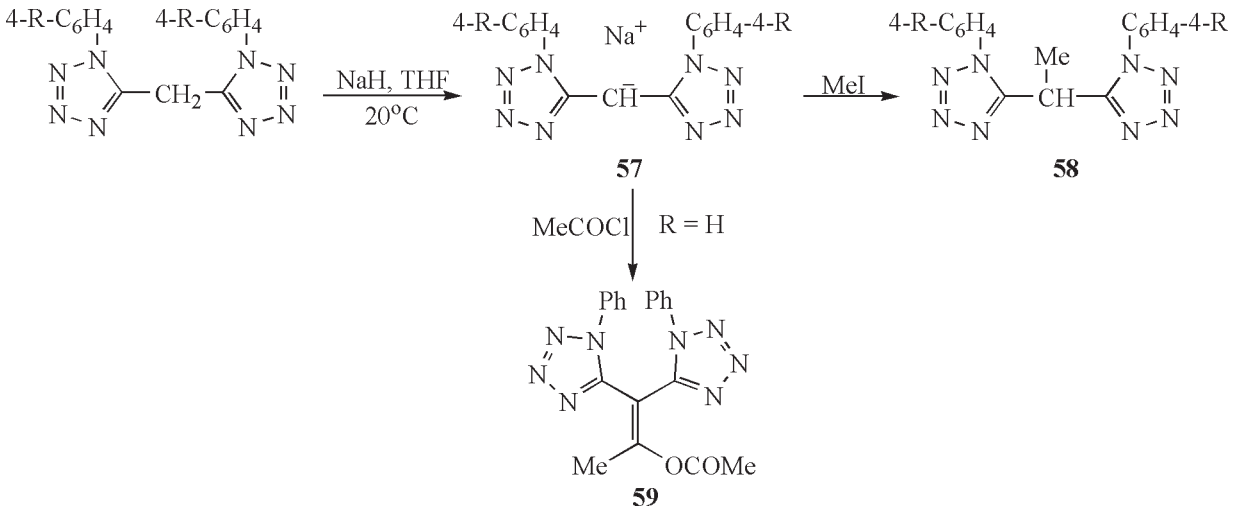
N-tert-butyl-5-(2-bromophenyl)tetrazole [49]. It cleanly undergoes transmetallation when treated with zinc chloride, and thus obtained zinc derivative **49** is the key compound in the synthesiss of another antihypertensive drug Tasosartan **50** [48].

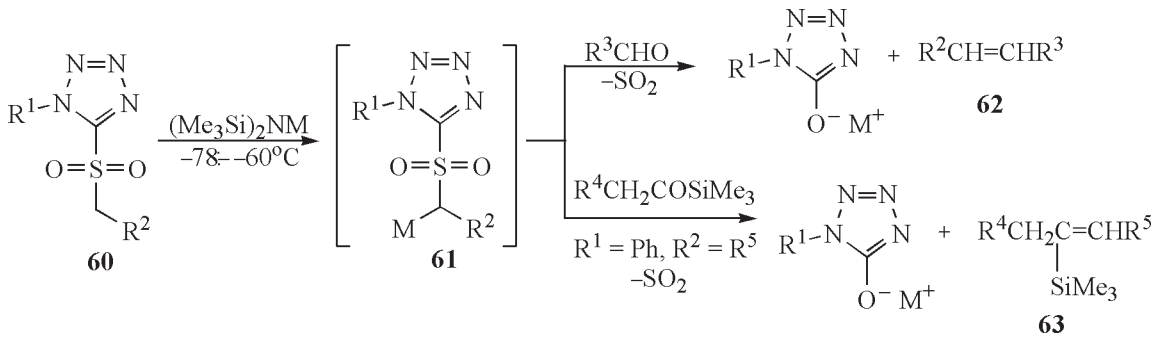
5-Methyl-2-triphenylmethyltetrazole **51** was lithiated with butyllithium at the methyl group. The corresponding lithium derivative under the action of electrophilic agents afforded in high yields functionally 5-substituted tetrazoles **52** [R = Ph (76%), PhCH=CH (72%), C_6H_{13} (71%)], **53** [R' = Bu (65%), Bz (73%), cyclo-C_6H_{11} (53%), Me_3Si (62%)], 54 (42%), 55 (45%), 56 (50%) where the trityl group is easily removed by treating with acids. Therefore the path of tetrazole **51** conversions involving its synthesis from 5-methyltetrazole, lithiation, condensation, and removal of the trityl group is a sufficiently convenient method of 5-methyltetrazole functionalization [50].

Bis(1-aryl-5-tetrazolyl)methane in a quantitative yield gives reaction products with sodium hydride in THF at room temperature. The arising crystalline salts have structure **57** as confirmed by their conversions at treatment with methyl iodide and acetyl chloride resulting in bistetrazoles **58** [R = H (93%), Me (91%)] and **59** (45%) [51].

1-substituted 5-alkylsulfonyltetrazoles **60** are metallated with alkaly metals hexamethyldisilylamides at



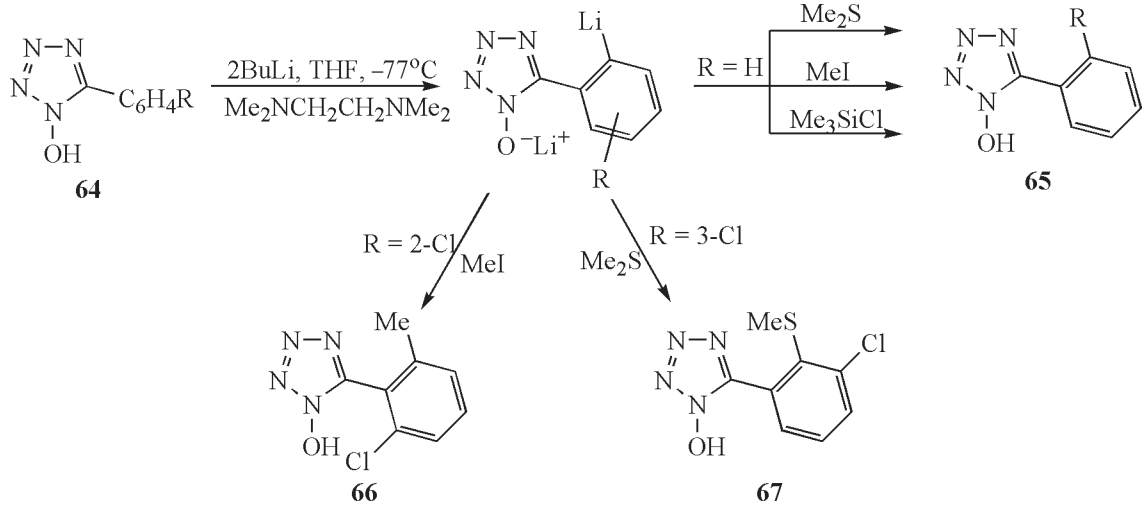




R^1 = *t*-Bu, Ph; R^2 = CH(Me)C_5H_{11}, Bu, CH=CH_2, Ph; R^3 = C_5H_{11}, cyclo-C_6H_{11}, C_9H_{19}, Ph; R^4 = $PhCH_2$, $Ph(CH_2)_2$; R^5= $Ph(CH_2)_2$, $C_{11}H_{23}$; M = Li, Na, K.

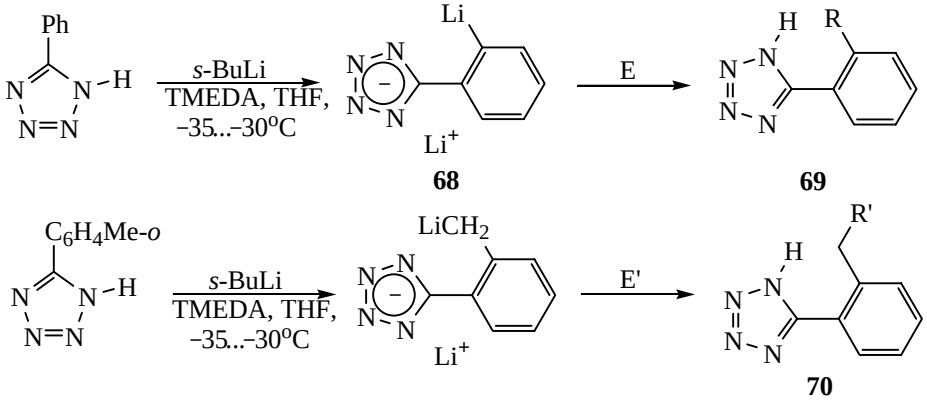
the carbon atom directly linked to sulfur. Metal derivatives thus obtained **61** in reaction with aldehydes give rise to 1-substituted 5-hydroxytetrazoles salts and 1,2-disubstituted alkenes **62** [52, 53]. Alongside the high yields (up to 100%) of alkenes **62** the process is characterized by a high streoselectivity. Therefore compounds **61** were recently extensively used in Julia olefination instead of aryl and hetaryl sulfones [5, 54] for stereoselective prepara-tion of naturally occurring compounds containing in their structure a fragment of trans-1,2-disubstituted alkene, for instance, Hennoxazole A [55], Herboxidiene [56], Thiazinotrienomycin E [57], Cylindrocyclophanes A and F [58], Zampanolide [59], Ambruticin [60], Laulimalide [61], Nafuredin [62], Callystatin A [63], Plakortone D [64], Brefeldin A [65], Lasonolide A [66, 67], Amphidino-lide A [68], Zampanolide, Dactylolide [69], Leuca-scandrolide A [70], Ionomycin [71], Borrelidin [72], Cycloviracin B1 [73], Microcarpalide [74], Oximidine III [75], Plakortone G [76]. The reaction of tetrazoles **61** (R^1 = Ph) with acyltrimethylsilanes was developed as an efficient preparation method for vinylsilanes **63** (yields up to 93%) [77].

Lithiation of 1-hydroxy-5-aryltetrazoles **64** required a double quantity of butyllithium because of the acid character of the hydroxy group. The reaction should also be carried out in the presence of TMEDA. In this case the lithiation occurred both at the hydroxy group andt the *ortho*-carbon of the phenyl. However the further reaction of the electrophilic reagents took place only at the phenyl group that was used in the synthesis of tetrazoles **65** [R = Me (83%), MeS (85%), Me_3Si (62%)], **66** (68%), **67** (80%) [78].



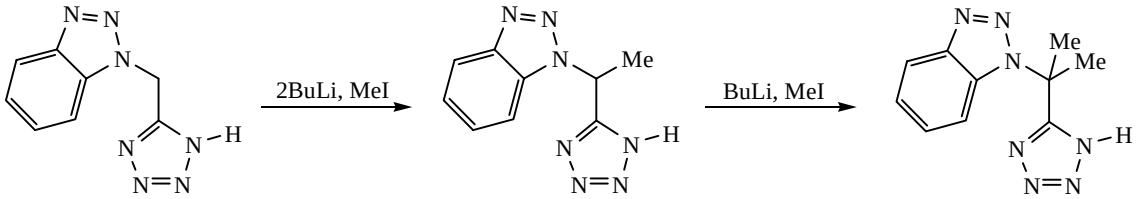
The lithiation of 5-monosubstituted tetrazoles also required excess of metallating agent for the reaction occurred at the hydrogen atom attached to nitrogen. The treatment of 5-phenyltetrazole with three equiv. of secondary butyllithium and one equiv. of TMEDA in THF furnished dilithium derivative **68** which with methyl iodide, acetaldehyde, or acrolein formed products of alkylation into the *ortho* position of the phenyl group **69**. Under similar conditions the 5-(2-tolyl)tetrazole reacted at the methyl group giving rise to compound **70** [79, 80].

5-(Benzotriazol-1-ylmethyl)tetrazole **71** was lithiated with excess butyllithium followed by the treatment with



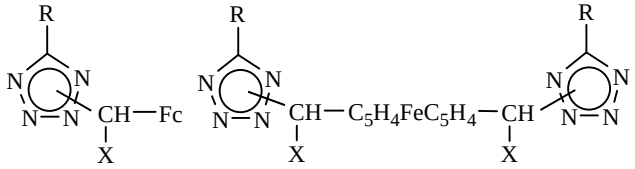
E = MeI, MeCH=O, VinCHO; **69**, R = Me (78%), MeCH(OH) (95%), VinCH(OH) (51% [79], 69% [80]); E' = MeI, $Me(CH_2)_4I$, BzBr, AllBr, $BrCH_2C(Me)=CH_2$, 3-Br-*cyclo*-C_6H_9; **70**, R^1 = Me (71%), $Me(CH_2)_4$ (92%), Bz (73%) [79], $AllCH_2$ (90%), $(CH_2)_2C(Me)=CH_2$ (83%), CH_2-*cyclo*[$CH(CH_2)_3CH=CH$] [80].

methyl iodide to furnish a product of the methylene group alkylation **72** (92%). The further lithiation and alkylation of compound **72** proceeded at the same position to provide dimethylation product in a 72% yield [81].



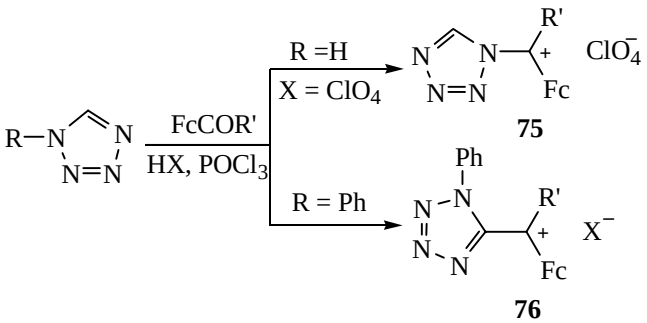
3.2. *Ferrocenyltetrazoles and Other Tetrazoles with a Metal–Carbon π-Bond*

The metal atom in the organometallic tetrazole derivatives can be linked to the carbon atom of the substituent not only by a σ-bond, but also with a π-bond. Among these compounds the ferrocenyl tetrazole derivatives are the best documented. They are prepared by alkylating the tetrazole substrate with α-halolkyl-ferrocenes and α-ferrocenylalkanols. These reagents alkylate the 5-R-tetrazoles or the corresponding salts in neutral or acid media to afford isomeric *N*-(α-ferrocenylalkyl)-5-R-tetrazoles. By this procedure tetrazoles **73** and **74** were obtained [82–85].



R = H, Me, Ph, NO_2, NH_2; X = H, Alk; Fc = $C_5H_4FeC_5H_5$.

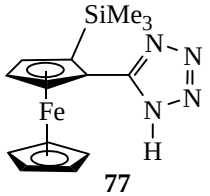
Another way of introducing the ferrocenyl moiety into the tetrazole structure consists in reaction of the latter with the formyl- and acetylferrocene in the presence of perchloric or tetrafluoroboric acid in the phosphorus oxychloride environment. Thus were recently synthesized salts of 1-α-ferrocenylalkyltetrazole **75** and 1-phenyl-5-α-ferrocenylalkyltetrazole **76** [86]. The formation of 5-substituted tetrazoles **76** in this process is of synthetic and fundamental importance for the tetrazole chemistry since it is a rare example of direct introduction of a substituent into the C^5 position of N-monosubstituted tetrazoles.



75, R' = H (76%), Me (52%); **76**, R' = H, X = ClO_4 (65%); R' = Me, X = ClO_4 (48%); R' = H, X = BF_4 (40%).

Ferrocenyltetrazoles can be prepared also by the classic tetrazole synthesis via heterocyclization of polynitrogen substrates involving a ferrocenyl substituent. For instance, optically active 5-substituted tetrazole **77**

was obtained in 81% yieldîì from the corresponding nitrile and sodium azide in the presence of tributyltin chloride [87].



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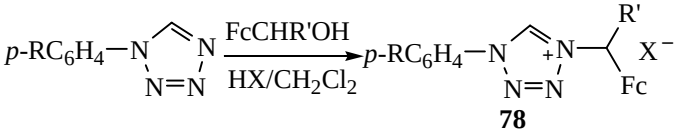
The synthesis of tetrazolium salts containing in the structure a ferrocenyl substituent is performed by quaternization of tetrazoles with α-ferrocenylalkanols or with vinylferrocene in a two-phase system dichloromethane–water solution of an inorganic acid. By this procedure from 1-aryltetrazoles 1-aryl-4-ferrocenylalkyltetrazolium salts **78** were obtained, and from unsubstituted tetrazole uncommon tetrazolium salts **79** were prepared with a hydrogen atom attached to a nitrogen. The latter was readily eliminated by treatment with bases to obtain 1- and 2-ferrocenylalkyltetrazoles **80** [85].



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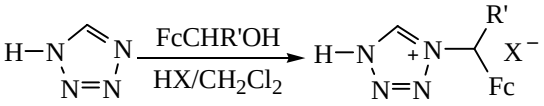

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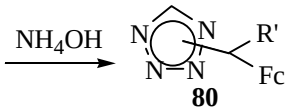
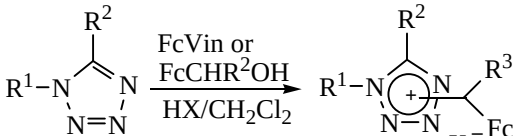


80

78, R = R' = H, X = BF_4 (93%), ClO_4 (74%); R = Me, R' = H, X = BF_4 (87%); R = Br, R' = H, X = BF_4 (79%); R = H, R' = Me, X = BF_4 (53%); R = NO_2, R' = Me, X = BF_4 (48%); R = H, R' = Ph, X = BF_4 (38%); 79, R' = H, X = BF_4 (59%), ClO_4 (63%); R' = Me, X = BF_4 (42%); R' = Ph, X = BF_4 (32%).

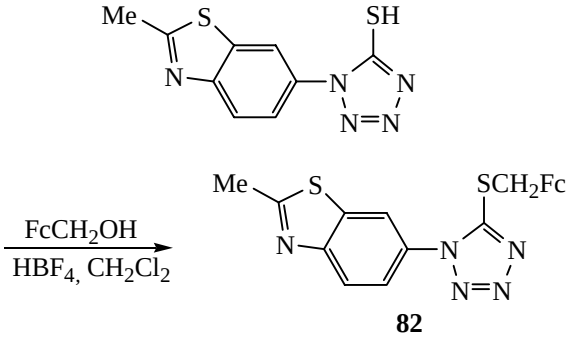
1,5-Disubstituted tetrazole furnish under similar conditions mixtures of salts of 1,3- and 1,4-trisubstituted tetrazolium **81** [88].



81

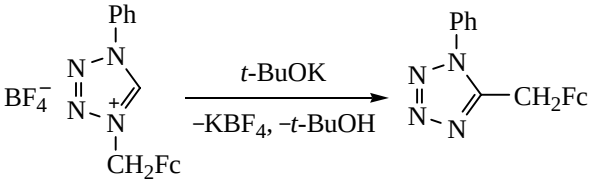
R^1 = Ph; R^2 = Me, Ph; R^1, R^2 = $(CH_2)_5$; R^3 = H, Me, Ph; X = ClO_4, BF_4.R^1 = Ph, R^2 = Me; R^1, R^2 = $(CH_2)_5$; R^3 = OMe, OEt, SCN, *p*-$MeC_6H_4SO_2$, $P^+Ph_3BF_4^-$, $CH(COPh)_2$, $NC_5H_5^+BF_4^-$.

At the same time the 5-mercpto-1-(2-methylbenzothiazol-6-yl)tetrazole under similar conditions yielded not the product of quaternization at a nitrogen atom of the tetrazole ring (tetrazolium salt), but 1,5-disubstituted tetrazole **82** resulting from the α-ferrocenylmethylation at the exocyclic sulfur [89].



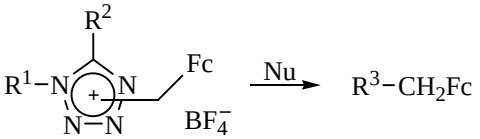
82

Among the transformations of the ferrocenylalkyltetrazolium salts a migration of ferrocenylalkyl group from the N into C-position first observed recently should be mentioned. It occurs in reaction of 1-phenyl-4-ferrocenylmethyltetrazolium tetrafluoroborate **83** with potassium *tert*-butylate in dioxane furnishing 1-phenyl-5-ferrocenylalkyltetrazole in a 52% yield [85]. This rearrangement resembles the Stevens rearrangement known with quaternary ammonium salts, and it is obviously interesting for functionalization tetrazoles in the position *5* of the ring.



83

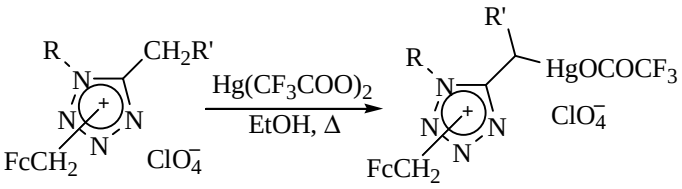
Salts **84** under treatment with nucleophilic reagents (Nu = alkalis, pyridine, triphenylphosphine, sodium thiocyanate, sodium *para*-toluenesulfinate, dibenzoylmethane) suffer dealkylation to afford in high yields 1,5-disubstituted tetrazoles and products of ferrocenylmethylation. Therefore these salts were suggested as reagents for introduction of ferrocenylalkyl group into various structures [88].



84 **85**

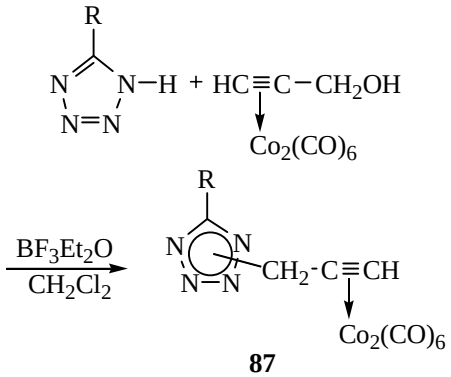
Analogous salts undergo mercuration with mercury(II) trifluoroacetat in ethanol at the α-carbon linked to the

endocyclic carbon atom affording bimetallic derivatives **86** [R = Ph, R' = H, 56%; R, R' = $(CH_2)_5$, 44%] [88].



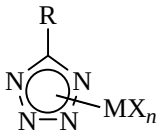
86

Finally, we like to mention in this section the synthesis of *N*-(hexacarbonyldicobalt-2-propynyl)tetrazoles **87**



87

including in the structure a π-coordinated cobalt atom. These compounds were obtained recently by metallopropargylation of tetrazole and 5-phenyltetrazole with hexacarbonyldicobalt-1-propynol. The reaction with tetrazole carried out in dichloromethane in the presence of boron trifluoride etherate gives rise to a compound that is difficultly assignable to 1- or 2-isomer. 5-Phenyltetrazole under these conditions furnished a mixture of the corresponding disubstituted tetrazoles with 2,5-isomer prevailing [90].

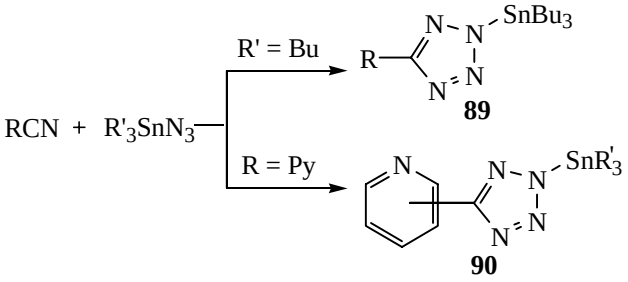


88

4. *N*-ORGANOTIN TETRAZOLES

Among the organometallic tetrazole derivatives compounds **88** should be distinguished where the metal is simultaneously linked to the tetrazole ring by an M–N bond and with another organic moiety by an M–C bond. Quite a number of these compounds was recently described where M = Al [91], Mn [92], Fe [93], Mo [94], Ru [95, 96], Rh [97], Pd [31], Hg [98], Tl [99], Sn [100–108]. The role of the X substituents is commonly played by alkenes, alkynes, CO, Ph, Cp, and their derivatives.

Nowadays the synthetic approaches to these compounds are known, and a number of these substances has been subjected to structural X-ray diffraction studies. At the same time their chemical reactions were poorly investigated save some individual instances. However these compounds are very promising as initial substrates not only in tetrazole synthesis but also in the chemistry of other nitrogen heterocycles. This is clear from the data on the chemical characteristics of the most well understood among compounds **88**, namely, of the corresponding organotin derivatives playing an important part in the preparative chemistry of tetrazoles.

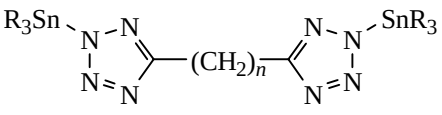


89

90

89, R = Ph, 1H-indol-3-yl, 1H-indol-3-yl(phenyl)methyl (60–80%) [100], 2-MeC_6H_4 (100%) [101], $Ph_3Sn(CH_2)_2$, $Ph_3Sn(CH_2)_3$ (97–100%) [102], $Ph_2P(CH_2)_m$ (*m* = 3, 4, 7) [103]; 90, *ortho*-, *meta*-, and *para*-isomers, R' = Et, Bu (47–88%) [104].

Tetrazole tin derivatives can be prepared by two procedures: either by addition of organotin azides to nitriles or by reaction of 5-monosubstituted tetrazoles with organotin oxides. The first method is preferable since it involves sufficiently accessible nitriles and azides and does not require a preliminary synthesis of tetrazoles. Therewith the necessary azides are often obtained *in situ* by reaction between sodium azide and trialkyltin chloride [100]. This procedure was used in the synthesis of a number of 5-aryl- and 5-hetaryl-*N*-(trialkylstannyl)tetrazoles **89** and **90** [100–104].

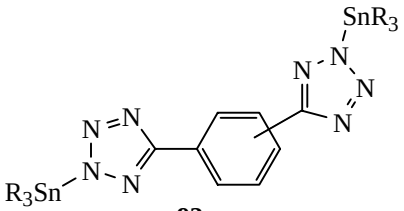


91

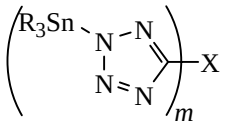
91, *n* = 1–6, R = Me, Et, *i*-Pr, Bu (13–65%) [105];

This method was also applicable to the preparation of bistetrazoles **91** and **92**, tris- and tetrakistrialkylstannyltetrazoles **93** [105–108].

The greatest practical opportunities are provided by organotin tetrazoles in the synthesis of 5-monosubstituted



92

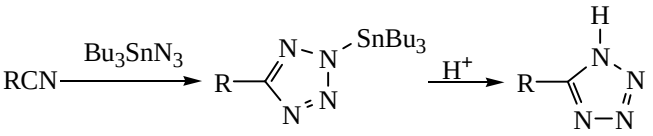


93

92, *ortho*-, *meta*-, and *para*-isomers, R = Me, Et, i-Pr, Bu (33–70%) [106]; 93, *m* = 3, X = $NO_2C(CH_2CH_2)_3$, 1,3,5-C_6H_3, R = Me, Et, Bu (42–70%) [107]; *m* = 4, X = $CHCH_2CH$, $C(CH_2CH_2)_2$, 1,2,4,5-C_6H_2, R = Et, Bu (24–80%) [108].

tetrazoles. At treatment of trialkyltin tetrazole derivatives with mineral acids the organotin moiety is replaced by a hydrogen. This process is often the final stage in the synthesis of 5-monosubstituted tetrazoles **94** from nitriles. The organotin derivatives arising in the first stage commonly are not isolated, and the reaction mixtures are directly treated with mineral acids [2, 3, 109–116].

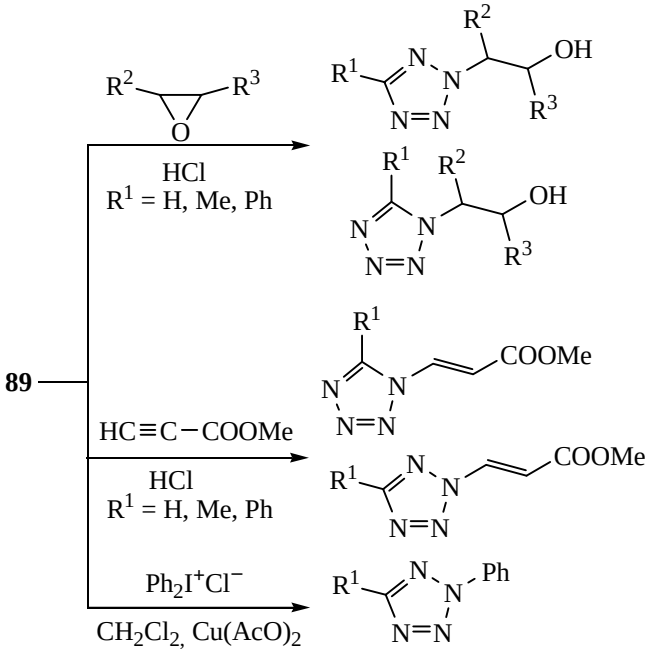
The available tributyltin azide is most commonly used as azide reagent. Recently the tris(2-perfluorohexylethyl)tin azide $(C_6F_{13}CH_2CH_2)_3SnN_3$ was tested in this process. The application of this reagent ensured high yields of 5-alkyl- and 5-aryltetrazoles **94** (up to 99%). The advantages of the reagent consist in the easily performed isolation of the target tetrazoles by extraction and in the recovery from the reaction mixture of the precursor of the azide agent, tris(2-perfluorohexylethyl)tin chloride [117].



94

The alkylation of 5-substituted 2-tributylstannyltetrazoles **89** was studied in some detail. As early as over 30 years ago the methylation of these compounds with various agents was shown to afford prevailingly 1,5-disubstituted tetrazoles [115, 116]. Recently the behavior of these tetrazoles was studied with respect to epoxides and methyl propiolate. The alkylation with these reagents resulted in mixtures of 1- and 2-substituted tetrazoles whose ratio essentially depended on the character of the R substituent. This behavior of the organotin derivatives is due to the association in solutions with a formation of an additional coordination bond at the N^4 atom [115]. At the same time 5-aryl- and 5-hetaryltetrazoles **89** readily react at room temperature with the diphenyliodonium chloride affording 2-phenyltetrazoles **95** (yield 34–70%) [118].

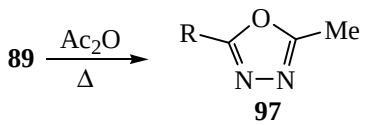
The alkylation of *ortho*- and *meta*-phenylene-bis(2-tributylstannyltetrazoles) **92** occurred less easily. In their reaction with a large excess (25:1) of α,ω-dibromoalkanes and α-bromo-ω-cyanoalkanes were obtained mainly the corresponding $N^{2,2'}$ and $N^{1,2'}$-substituted bromoalkyl- and cyanoalkyltetrazoles. The reaction of *ortho*-isomer **92** with tenfold excess of 1,2-dibromoethane in methanol successfully gave in a 37% yield $N^{1,1'}$-substituted cyclophane **96** [119].



95

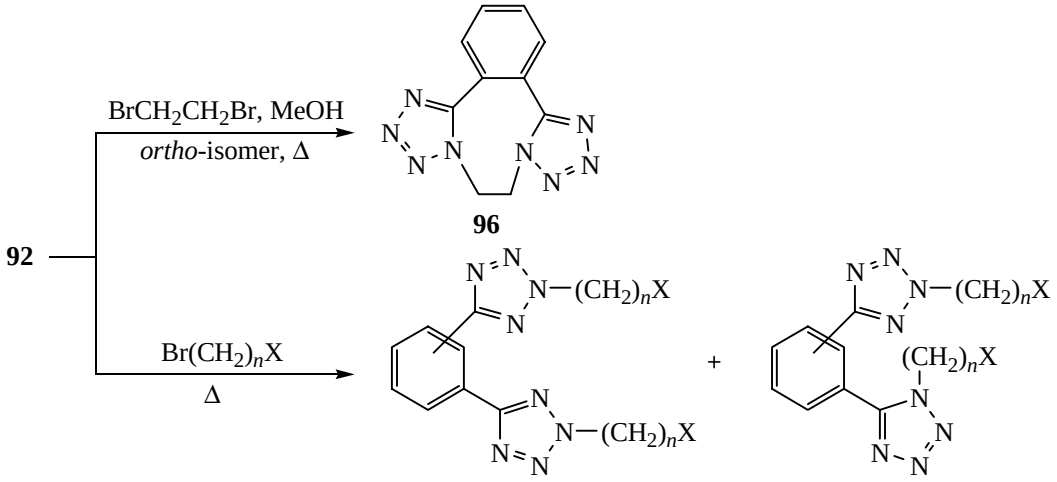
95, R^1 = Ph, *p*-MeC_6H_4, *p*-BrC_6H_4, 1*H*-indol-3-yl, 1*H*-indol-3-ylmethyl; R^2 = H, Ph; R^3 = H, Me, Ph, COOEt; R^2, R^3 = $(CH_2)_4$.

Like 5-monosubstituted tetrazoles, tetrazoles **89** at boiling with the acetic anhydride are converted into 2-R-5-methyl-1,3,4-oxadiazoles **97**. The reaction apparently



97

97, R = Ph (80%), 1-acetylindol-3-yl (57%), 1H-indol-3-yl-(phenyl)methyl (53%).



X = Br, CN; *n* = 2-8.

involves N-acyltetrazoles formation followed by recyclization [100].

CONCLUSIONS

The facts generalized in the present review demonstrate considerable recent advances in the chemistry of organometallic tetrazole derivatives. It should be first mentioned the significant extension of this compounds range both with involvement of various metals and tetrazoles. Furtheremore, these compounds already play the key role in the synthesis of various tetrazoles, among them difficultly accessible, by means of functionalizing simple tetrazoles. A definite trend arouse consisting in applying the metallized tetrazole to the synthesis of the other nitrogen-containing heterocycles and of naturally occurring compounds. The synthetic potential of compounds under consideration is far from being exhausted and calls for further investigations.

Nonetheless, many gaps exist in the chemistry of tetrazole organometallic derivatives regarding the poor data on the properties of the tetrazole derivatives of most metals and the lack of universal procedures for their synthesis. The analysis of the trends in the development of the studies in the area of organometallic tetrazoles shows the growing interest to these substances that promises the filling of the existing gaps and discovery of new application for the compounds.

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