New approaches to synthesis of tris[1,2,4]triazolo[1,3,5]triazines

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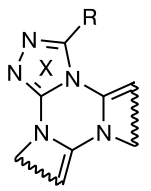
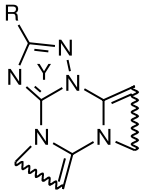
Thermal cyclization of 3-R-5-chloro-1,2,4-triazoles (R = Cl, Ph) afforded 2,6,10-tri-R-tris[1,2,4]triazolo[1,5-*a*:1′,5′-*c*:1″,5″-*e*][1,3,5]triazines **5** (R = Ph) and **7** (R = Cl). These compounds are first representatives of this class of heterocycles, whose structures were unambiguously established. Treatment of these compounds with nucleophiles (H_2O/NaOH, NH_3) results in the triazine ring opening to give compounds consisting of three 1,2,4-triazole rings linked in a chain. For example, treatment of cyclic compound **5** with aqueous alkali affords 3-phenyl-1-{3-phenyl-1-(3-phenyl-1*H*-1,2,4-triazol-5-yl)-1,2,4-triazol-5-yl}-1*H*-1,2,4-triazol-5-one. Treatment of 3,7,11-triphenyltris[1,2,4]triazolo[4,3-*a*:4′,3′-*c*:4″,3″-*e*][1,3,5]triazine (**2**) with HCl/$SbCl_5$ leads to the triazine ring opening giving rise to 5-(3-chloro-5-phenyl-1,2,4-triazol-4-yl)-3-phenyl-4-(5-phenyl-1*H*-1,2,4-triazol-3-yl)-1,2,4-triazole. Thermal cyclization of the latter produces 3,7,10-triphenyltris[1,2,4]triazolo[1,5-*a*:4′,3′-*c*:4″,3″-*e*][1,3,5]triazine (**13**). Thermolysis of both cyclic compound **2** and cyclic compound **13** is accompanied by the Dimroth rearrangement to yield 3,6,10-triphenyltris[1,2,4]triazolo[1,5-*a*:1′,5′-*c*:4″,3″-*e*][1,3,5]triazine (**14**). Compounds **13** and **14** are the first representatives of cyclic compounds with this skeleton. ^{13}C NMR spectroscopy allows the determination of the isomer type in a series of tris[1,2,4]triazolo[1,3,5]triazines.

Key words: fused heterocycles, nitrogen heterocycles, 1,2,4-triazoles, 1,3,5-triazines, tris[1,2,4]triazolo[1,3,5]triazine, pyrolysis, Dimroth rearrangement, synthetic methods.

The 1,2,4-triazole ring can be fused to the 1,3,5-triazine ring in two ways to give the structure **A** or **B**. Let us denote the 1,2,4-triazole ring involved in the structures **A** and **B** as the X ring and Y ring, respectively. Tris[1,2,4]triazolo[1,3,5]triazine in which the triazine ring is fused to three triazole rings is designated as TTT.



A



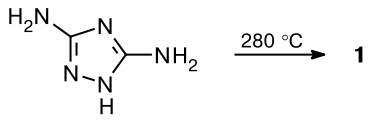
B

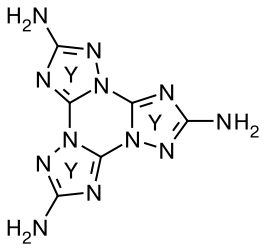
In the early 20th century, the first tris[1,2,4]triazolo[1,3,5]triazine was prepared by heating 3,5-diamino-1,2,4-triazole (guanazole).[1] The authors of the cited paper[1] assigned structure Y_3-TTT **1a** to this compound (Scheme 1) and called it pyroguanazole. More recently, structure X_3-TTT **1b** was proposed[2] for this compound based on its chemical behavior. However, the assignment is not conclusive and, in essence, the choice between structures **1a** and **1b** was not made.

Triphenyl-substituted compound **2** with the structure X_3-TTT was prepared by Huisgen *et al.*[3] by the reaction of cyanuric chloride with 1-phenyltetrazole (Scheme 2). The reaction mechanism involving the intermediate formation of nitrile imine **C** unambiguously determines the X_3 structure of compound **2**, and the relatively low thermolysis temperature excludes the possibility of a skeletal rearrangement (for details, see below).

To our knowledge, the above compounds are the only known tris[1,2,4]triazolo[1,3,5]triazines.

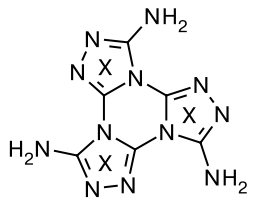
Scheme 1





Y_3-TTT **1a**

or



X_3-TTT **1b**

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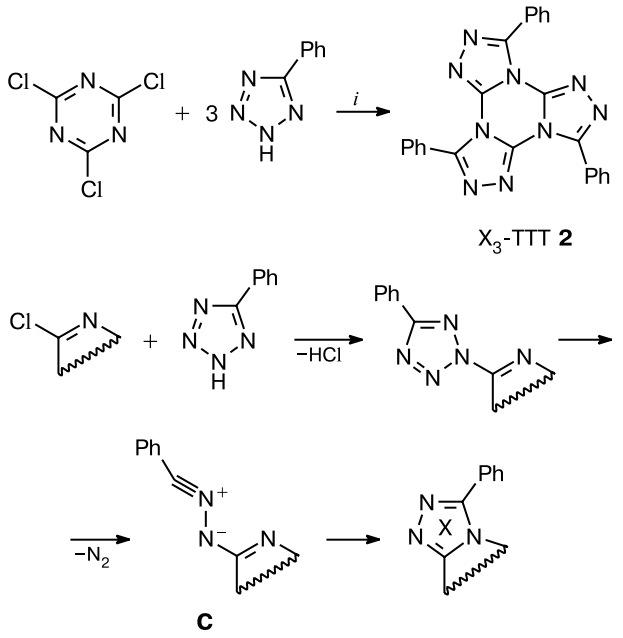
Scheme 2



i. Toluene, reflux.

The aim of the present study was to develop new procedures for the synthesis of tris[1,2,4]triazolo[1,3,5]triazines, which differ in the mutual arrangement of the triazole rings. This class of compounds is of interest from the standpoint of their biological activity and also because they are potential components of materials with high thermal stability.

Synthesis of Y_3-TTT

By analogy with the Hofmann—Erhart method,[1] we attempted to synthesize triphenyl-substituted TTT by pyrolysis of 5-amino-3-phenyl-1,2,4-triazole (**3a**). However, this attempt was unsuccessful. Heating of 5-methylthio-3-phenyl-1,2,4-triazole (**3b**) also did not give the desired result. Pyrolysis of 5-chloro-3-phenyl-1,2,4-triazole (**4**) afforded compound **5** with the Y_3 structure.*

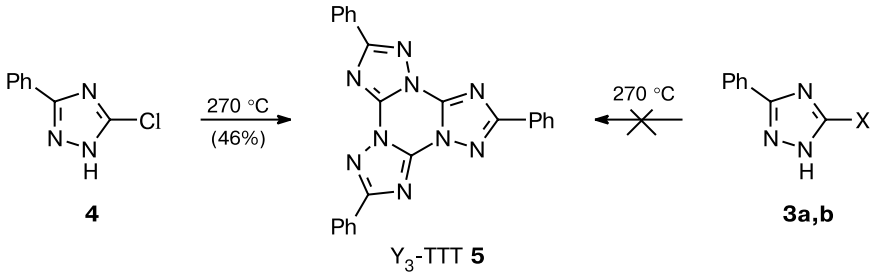
The best results were obtained upon heating of triazole **4** without a solvent at 230—270 °C (the yield of **5** was 46%). Heating in sulfolane at the same temperature afforded compound **5** in lower yield (12%). Under thermolysis conditions, TTT **5** is stable. Compound **5** begins to decompose during melting only at about 400 °C.

For thermolysis of 5-chloro-3-phenyl-1,2,4-triazole **4** to form TTT with the Y_3 structure, it is necessary that the N(1) atom of triazole be the attacking nucleophile both in the first and second steps of the reaction, and the N(1) atom of the intermediate linear trimer be the attacking nucleophile in the third step (Scheme 4).

It should be noted that the mechanism involving the initial formation of X_3-TTT **2** followed by its rearrange-

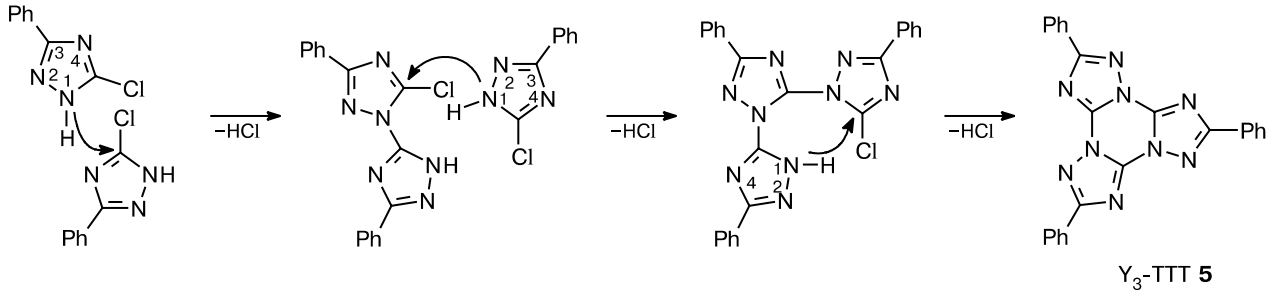
* Examples of thermal trimerization of imidazoles and pyrazoles containing the chlorine atom[4,5] or the methylthio group[6] were described in the literature.

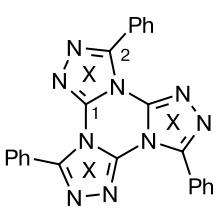
Scheme 3



3: X = NH_2 (**a**), SMe (**b**)

Scheme 4





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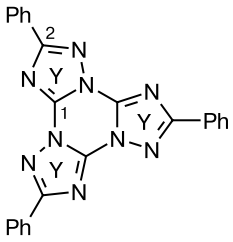

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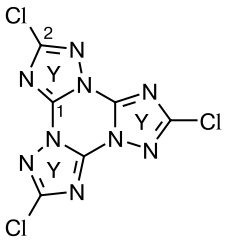

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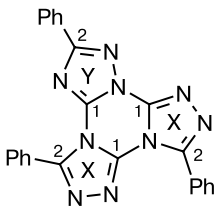

13

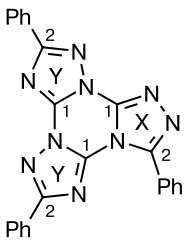

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Table 1. ^{13}C NMR spectroscopic data for TTT (DMSO-d_6)

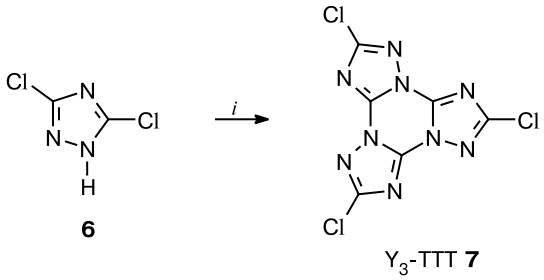
Compound	δ (*J*/Hz)					
	C(1)	C(2) X ring	C(2) Y ring	Ph		
				ipso	*ortho*, *meta*	*para*
2	141.9	149.2 $^3J = 4.5$	—	124.6	128.5, 129.8	131.4
5	145.5	—	162.8 $^3J = 4.0$	128.2	126.8, 129.0	131.1
7	145.6	—	157.4	—	—	—
13	142.3, 142.7, 143.8	148.8, 149.4	161.9	124.3, 124.7, 128.2	126.7, 128.5, 128.6, 129.3, 129.9, 130.1	131.4, 131.5, 131.7
14	143.1, 144.3, 144.9	148.7	161.9, 162.8	124.4, 128.1, 128.3	126.6, 126.8, 128.4, 129.3, 129.9	131.3, 131.4, 131.5

* Two superimposed signals.

ment into Y_3-TTT **5** can be excluded because this rearrangement (as demonstrated below) occurs at higher temperature.

Thermal cyclization appeared to be suitable also for the synthesis of trichloro-substituted Y_3-TTT **7**. This compound was prepared in 17% yield by heating 3,5-dichloro-1,2,4-triazole **6** in the absence of a solvent at 240—270 °C. Heating in sulfolane led to an increase in the yield to 20%. The latter procedure is preferable also because it makes isolation of the product easier. Compound **7** crystallizes in pure form upon cooling of the reaction mixture to room temperature. Trichloro-substituted TTT **7**, like triphenyl-substituted TTT **5**, is thermally stable (m.p. 311—313 °C, without decomposition).

Scheme 5



6 $\xrightarrow{i}$ Y_3-TTT **7**

i. 240—270 °C, sulfolane (20%).

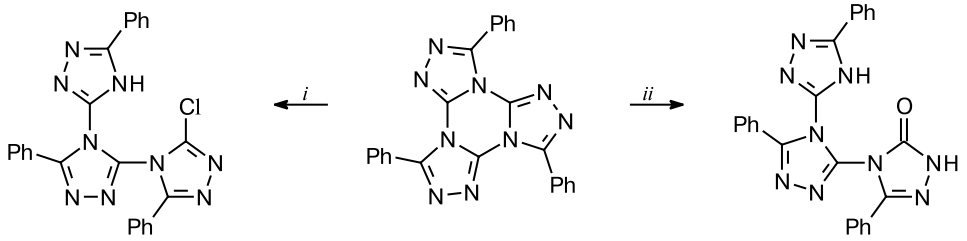
In addition to TTT **7**, thermolysis in the absence of the solvent afforded two groups of products, which were isolated by chromatography. The ^{13}C NMR spectra demonstrate that the first group consists of four main compounds. The spectrum of each compound shows two signals for carbon atoms at δ 145—146 and 154—158 (all signals of the mixture of four compounds, δ: 145.2, 145.5, 145.8, 146.0, 154.7, 156.0, 157.5, 157.6). These chemical shifts are similar to those of Y_3-TTT **7** (Table 1). We believe that these compounds are macrocyclic analogs of trimer **7**, which is confirmed by the fact that their mass spectra have signals of both the tetramer (*m/z*: 404 $[M]^+$) and the pentamer (*m/z*: 470 $[M - Cl]^+$). The second group of products consists, presumably, of trimeric cyclic compounds **7**, in which one, two, or three chlorine atoms are replaced by the 3,5-dichloro-1,2,4-triazole fragment. This is evidenced by the fact that the mass spectrum of these compounds has peaks at *m/z*: 404 $[M]^+$, 505 $[M]^+$, 606 $[M]^+$.* These compounds could most likely be formed directly by cyclization of the corresponding linear chains rather than by the replacement of the chlorine atoms in cyclic compound **7**.

Triazine ring opening in TTT

The chemical properties of triphenyl-substituted X_3-TTT **2** differ substantially from those of Y_3-TTT **5**.

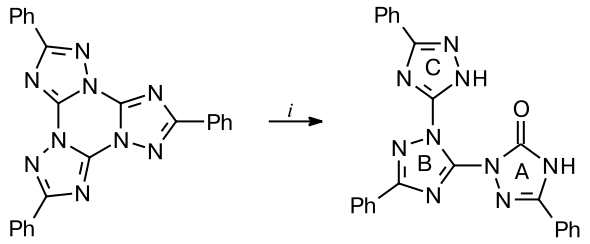
* Only signals with the ^{35}Cl isotope are given.

Scheme 6



Reagents, conditions, and yields of products: *i*. HCl/$SbCl_5$, dioxane, reflux, 83% yield; *ii*. H_2O/NaOH or H_2O/HCO_2H, yield >90%.

Scheme 7



i. H_2O/NaOH, 77% yield

Compound **2** is more reactive and is relatively easily hydrolyzed in both alkaline and acidic media, resulting in the triazine ring opening to form triazolone **8** (Scheme 6). An interesting fact is that the triazine ring of X_3-TTT **2** is opened with HCl in the presence of $SbCl_5$ as the catalyst to form chloro-substituted compound **9**. It should be noted that an attempt to prepare this compound by treatment of triazolone **8** with phosphorus(v) oxychloride failed.

Compound **5** is stable to acidic hydrolysis and to the action of HCl/$SbCl_5$ and gives triazolone **10** only in the presence of an alkali.

Compound **7**, like compound **5**, is stable to acidic hydrolysis and forms triazolone **11** only in the presence of an alkali, the reaction proceeding under milder conditions than those of triphenyl-substituted TTTs **2** and **5**. The triazine ring opening in Y_3-TTT **7** occurs also in the presence of ammonia to form compound **12**.

To our knowledge, compounds consisting of three triazole rings linked in a chain (compounds **8**—**12**) have not been described earlier.

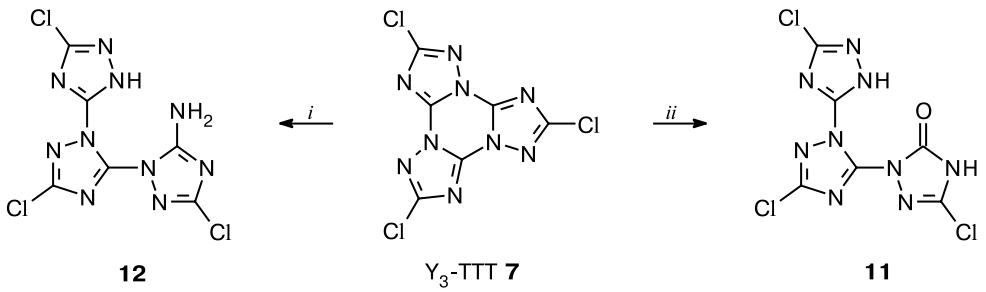
Synthesis of X_2Y-TTT and XY_2-TTT

To prepare phenyl-substituted X_2Y-TTT **13** containing three triazole rings (two X rings and one Y ring), we attempted to perform cyclization of compounds **8** and **9**. Triazolone **8** appeared to be an inert compound. The addition of a concentrated alkali, refluxing in $POCl_3$, or heating at 350 °C did not lead to cyclization of **8**. By contrast, chloro derivative **9** undergoes smooth cyclization at 240 °C to form compound X_2Y-TTT **13** (Scheme 9). An attempt to prepare this compound by the rearrangement of X_3-TTT **2** failed. The latter compound remained unchanged upon prolonged storage at 240 °C.

Heating of X_2Y-TTT **13** at higher temperature (350 °C) afforded XY_2-TTT **14** containing two triazole Y rings. This compound was also prepared directly from X_3-TTT **2** by heating at 350 °C. Under these conditions, the reaction produced also trace amounts of Y_3-TTT **5** (TLC data), in which all three triazole rings are rearranged.

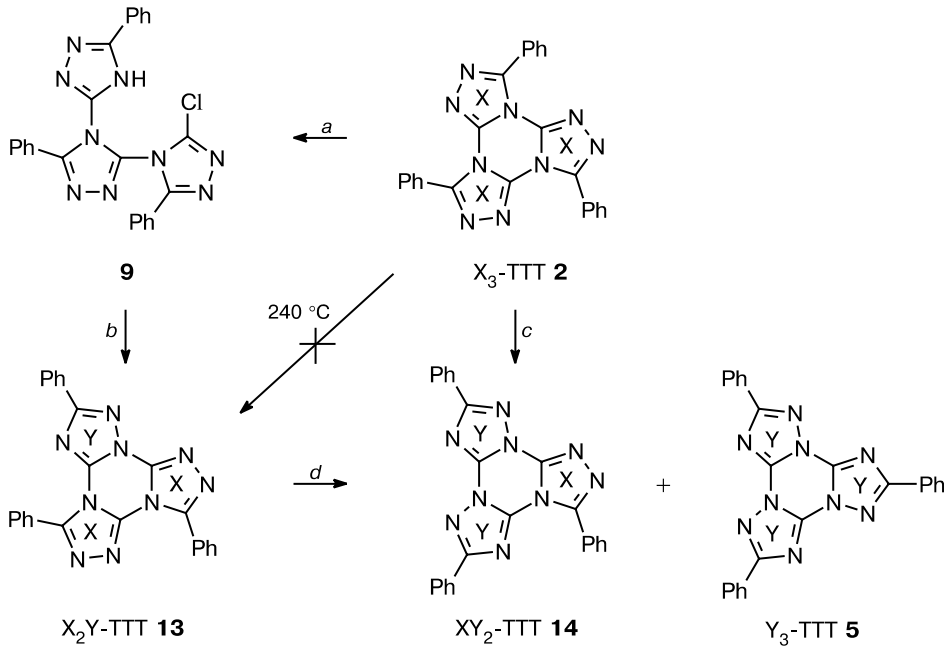
The transformation of the triazole X ring into the Y ring can be assigned to the Dimroth rearrangement.[7] However, the mechanism of the rearrangement involving the

Scheme 8



Reagents, conditions, and yields of products: *i*. NH_3, dioxane, 83% yield; *ii*. H_2O/NaOH, 61% yield.

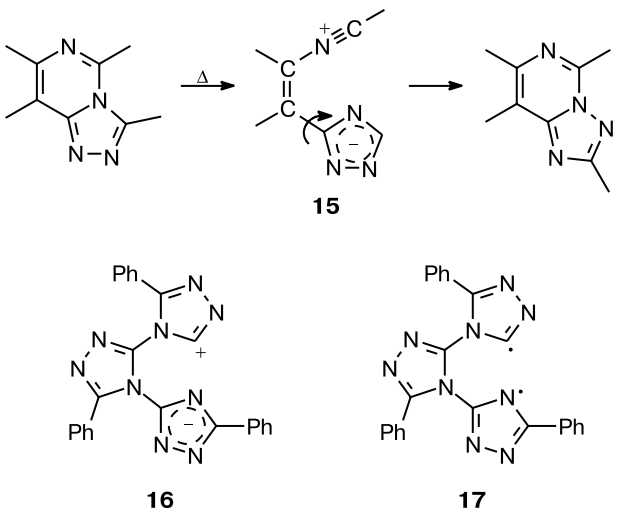
Scheme 9



Reagents, conditions, and yields of products: *a*. HCl/$SbCl_5$, dioxane; *b*. 240 °C, 71% yield; *c*. 350 °C, 80% yield; *d*. 350 °C, yield >95% **14**, trace amounts of **5**.

cleavage of the bond between two heterocycles has not, to our knowledge, been described in the literature. The thermal Dimroth rearrangement for structures similar to those under study generally occurs at temperatures below 250 °C. The proposed mechanism involves the ionic cleavage of the C—N bond to form intermediate **15**, in which both the cationic and anionic parts of the zwitterion are stabilized (Scheme 10).

Scheme 10



In the case under consideration, an analogous ionic bond cleavage would give rise to zwitterion **16**, whose positive charge cannot be well distributed. Taking into account also the high reaction temperature, the radical mechanism of the rearrangement involving the intermediate formation of biradical **17** cannot be ruled out as well.

Structure of TTT

^{13}C NMR spectroscopy is the most convenient method for establishing the structures of TTT systems. We carried out a comparative study of X_3-TTT **2** and Y_3-TTT **5**. The unambiguous assignment of the signals of these compounds was made based on the ^{13}C NMR spectra measured without proton decoupling (see Table 1). The signal for C(2) of the X triazole ring is observed at much higher field compared to the signal for C(2) of the Y triazole ring (TTT **5**). The difference between the chemical shifts is rather large ($\Delta\delta = 13.6$) and can be used to recognize the X and Y rings.

Actually, the ^{13}C NMR spectra of compounds **13** and **14** allowed us to unambiguously assign these two compounds to the X_2Y and XY_2 isomers, respectively (see Table 1).

Compound **7** can be unambiguously assigned to the Y_3 isomer based on the ^{13}C NMR spectrum taking into account the change in the chemical shift of the C(2) atom upon the replacement of the phenyl group with the chlorine atom (see Table 1).

This considerable difference in the chemical shifts of the signals for C(2) of the X and Y rings is clear if the X and Y rings are considered as the 4*H*-1,2,4-triazole and

1*H*-1,2,4-triazole derivatives, respectively. It is known[8] that the signal for C(3) in the spectra of the latter compounds appears at lower field compared to the signal for C(5).

* * *

To summarize, we developed a procedure for the synthesis of the Y_3-TTT system by thermal cyclization of 5-substituted 3-chloro-1,2,4-triazoles. The X_2Y-TTT and XY_2-TTT systems were synthesized for the first time. Systems consisting of three nonannulated triazole rings were prepared for the first time by the triazine ring opening in TTT using nucleophiles. The triazole X and Y rings of tris[1,2,4]triazolo[1,3,5]triazine can be distinguished with certainty by ^{13}C NMR spectroscopy.

Experimental

The IR spectra were recorded on a Perkin-Elmer 577 spectrometer. The mass spectra were obtained on a Kratos MS-30 instrument (EI, 70 eV); for the chlorine-containing fragments, only the signals with the ^{35}Cl isotope are given. The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer operating at 300.13 and 75.5 MHz, respectively. The assignment of the signals in the ^{13}C NMR spectra was made using spectra measured without proton decoupling, the INEPT and DEPT-135 experiments, and additive calculations. The reactions were monitored by TLC (Silufol UV-254) using silica gel for column chromatography.

3-Amino-5-phenyl-1,2,4-triazole (**3a**),[9] 3-methylthio-5-phenyl-1,2,4-triazole (**3b**),[10] 5-chloro-3-phenyl-1,2,4-triazole (**4**),[11] and 3,5-dichloro-1,2,4-triazole (**6**)[12] were prepared according to procedures described earlier.

3,7,11-Triphenyltris[1,2,4]triazolo[4,3-*a*:4′,3′-*c*:4″,3″-*e*]-[1,3,5]triazine (2). Compound **2** was synthesized according to a known procedure[3] and thoroughly dried at 120 °C *in vacuo*. ^1H NMR (DMSO-d_6), δ: 7.65 (m, 3 H); 8.05 (dd, 2 H, J = 1.9 Hz, J = 8.1 Hz). MS, *m/z*: 429 $[M]^+$.

2,6,10-Triphenyltris[1,2,4]triazolo[1,5-*a*:1′,5′-*c*:1″,5″-*e*]-[1,3,5]triazine (5). ***A.*** Chlorotriazole **4** (360 mg, 2 mmol) was heated at 230 °C for 0.5 h and then at 270 °C for 0.5 h. The reaction was accompanied by HCl elimination. Then the reaction mixture was cooled and washed on a filter with acetone (8 mL). Compound **5** was obtained in a yield of 130 mg (46%) as colorless crystals, m.p. 390—400 °C (with decomp.). Found (%): C, 67.31; H, 3.54; N, 29.27. $C_{24}H_{15}N_9$. Calculated (%): C, 67.13; H, 3.52; N, 29.35. IR (KBr), ν/cm^{-1}: 729, 1123, 1337, 1445, 1625. ^1H NMR (DMSO-d_6), δ: 7.66 (m, 3 H); 8.32 (dd, 2 H, $J \approx 3$ Hz, $J \approx 7$ Hz). MS, *m/z*: 429 $[M]^+$.

B. A solution of triazole **4** (300 mg, 1.7 mmol) in dry sulfolane (3 mL) was heated at 250 °C for 0.5 h and at 270 °C for 1 h. After cooling, the reaction mixture was poured into water (20 mL). The precipitate was filtered off and washed on a filter with acetone. Compound **5**, which was identical to that prepared above, was obtained in a yield of 30 mg (12%).

2,6,10-Trichlorotris[1,2,4]triazolo[1,5-*a*:1′,5′-*c*:1″,5″-*e*]-[1,3,5]triazine (7). ***A.*** A solution of triazole **6** (8 g, 58 mmol) in dry sulfolane (15 mL) was heated at 250 °C for 1 h and at 270 °C for 1 h. The reaction solution was cooled to 20 °C. After 6 h, the colorless crystals were filtered off and washed with a small amount of cold benzene. Compound **7** was obtained in a yield of 1.2 g (20%), m.p. 311—313 °C (from toluene). Found (%): C, 23.60; Cl, 34.84; N, 41.49. $C_6Cl_3N_9$. Calculated (%): C, 23.67; Cl, 34.93; N, 41.40. IR (KBr), ν/cm^{-1}: 716, 757, 1081, 1237, 1269, 1449, 1629. MS, *m/z*: 303 $[M]^+$.

B. Triazole **6** (190 mg, 1.4 mmol) was heated at 210—215 °C for 10 min, at 240 °C for 15 min, and at 270 °C for 25 min. The residue (140 mg) was separated by chromatography ($CHCl_3$ as the eluent). Compound **7**, which was obtained in a yield of 25 mg (17%), was identical to that described above.

3-Phenyl-4-[3-phenyl-4-(3-phenyl-1*H*-1,2,4-triazol-5-yl)-1,2,4-triazol-5-yl]-1*H*-1,2,4-triazol-5-one (8). ***A.* Acidic hydrolysis.** A solution of TTT **2** (100 mg, 0.23 mmol) in 86% formic acid (1 mL) was refluxed for 6 h (TLC control; acetone—hexane, 1 : 1, as the eluent). The solution was concentrated and the residue was dried at 80 °C *in vacuo* over P_2O_5. Triazolone **8** was obtained in a yield of 100 mg (96%) as colorless crystals, m.p. 158—160 °C (from toluene). Found (%): C, 64.18; H, 3.71; N, 28.66. $C_{24}H_{17}N_9O$. Calculated (%): C, 64.42; H, 3.83; N, 28.17. IR (KBr), ν/cm^{-1}: 1688, 1721 (C=O). ^1H NMR (DMSO-d_6), δ: 7.40—7.62 (m, 12 H); 7.84 (dd, 1 H, $J \approx 3$ Hz, $J \approx 7$ Hz); 7.93 (d, 2 H); 12.50 (s, 1 H, NH); 15.20 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 125.5, 125.79, 125.84 (3 *ipso*-Ph); 126.1, 126.6, 128.2, 128.7, 129.0, 129.2 (6 *o*- and *m*-Ph); 130.6, 130.8, 131.1 (3 *p*-Ph); 145.1 (^3J = 3.2); 153.6 (^3J = 5.2); 154.5 (3 C—Ph, ^3J = 4.2 Hz); 143.7, 151.0 (br.s, C=O), 155.6. MS, *m/z*: 446 $[M - 1]^+$.

***B.* Alkaline hydrolysis.** Compound **2** (100 mg, 0.23 mmol) was dissolved with heating in DMF (1 mL). A solution of NaOH (0.3 g) in water (0.3 mL) was added to the cold reaction solution. The reaction mixture was stirred for 0.5 h, poured into water with ice (20 g), and neutralized with concentrated aqueous HCl. The precipitate that formed was filtered off, washed with water, and dried *in vacuo* over P_2O_5. Compound **9** was obtained in a yield of 95 mg (92%). The product is identical to that prepared under acidic hydrolysis conditions.

5-(3-Chloro-5-phenyl-1,2,4-triazol-4-yl)-3-phenyl-4-(5-phenyl-1*H*-1,2,4-triazol-3-yl)-1,2,4-triazole (9). Antimony pentachloride (10 mg, 0.03 mmol) was added to a solution of **2** (100 mg, 0.23 mmol) in dry dioxane (3 mL). Gaseous HCl was passed through the refluxing reaction mixture for 3 h. Then a new portion of $SbCl_5$ (10 mg, 0.03 mmol) was added, and HCl was passed for 2 h. After consumption of the starting compound (TLC control; EtOAc—hexane, 3 : 1, as the eluent), the solution was cooled and the solvent was distilled off *in vacuo*. The residue was thoroughly washed with ice water (20 mL) and extracted with $CHCl_3$ (30 mL). The extract was dried with $MgSO_4$ and the solvent was distilled off *in vacuo*. The residue was dried *in vacuo* at 80 °C over P_2O_5. Compound **9** was obtained in a yield of 90 mg (83%) as colorless crystals, m.p. 217—218 °C (from acetone). Found (%): C, 61.59; H, 3.30; Cl, 7.90; N, 26.68. $C_{24}H_{16}ClN_9$. Calculated (%): C, 61.87; H, 3.46; Cl, 7.61; N, 27.06. ^1H NMR (DMSO-d_6), δ: 7.45—7.57 (m, 11 H); 7.65 (d, 2 H, J = 6.9 Hz); 7.77 (dd, 2 H, $J \approx 3$ Hz, $J \approx 7$ Hz); 12.00 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 124.5, 124.8, 125.5 (3 *i*-Ph); 126.1, 127.1, 128.3 (3 *o*-Ph); 128.8, 129.2* (3 *m*-Ph); 131.2*, 131.3 (3 *p*-Ph); 142.3, 142.7, 150.3 (br.s); 155.0 (^3J = 4.2 Hz); 155.4 (^3J = 4.0 Hz); 155.9 (br.s). MS, *m/z*: 429 $[M - HCl]^+$.

3-Phenyl-1-[3-phenyl-1-(3-phenyl-1*H*-1,2,4-triazol-5-yl)-1,2,4-triazol-5-yl]-1*H*-1,2,4-triazol-5-one (10). Compound **5** (100 mg, 0.23 mmol) was dissolved in a minimum amount of hot DMF. A solution of NaOH (3 g) in water (4 mL) was added to the reaction solution cooled to 30 °C. The reaction mixture was stirred for 20 min, poured into ice water (50 mL), and neutralized with a concentrated aqueous HCl solution. The precipitate was filtered off, the filtrate was extracted with EtOAc (2×20 mL), and the extract was dried with $MgSO_4$. After evaporation of the solvent, the residue was combined with the precipitate that remained after filtration, and the mixture was washed with water and dried *in vacuo* at 100 °C over P_2O_5. Compound **10** was obtained in a yield of 90 mg (77%), m.p. 296—299 °C (from a EtOH—H_2O mixture, 5 : 1). Found (%): C, 64.09; H, 4.07; N, 28.24. $C_{24}H_{17}N_9O$. Calculated (%): C, 64.42; H, 3.83; N, 28.17. IR (KBr), ν/cm^{-1}: 1720 (C=O). ^{1}H NMR (DMSO-d_6), δ: 7.50—7.62 (m, 9 H); 7.88 and 7.98 (both m, 2 H each); 8.16 (d, 2 H, J = 6.8 Hz); 12.50 and 12.90 (both br.s, 1 H each, NH). ^{13}C NMR (DMSO-d_6), δ: 125.7, 126.3, 129.4 (3 *i*-Ph); 125.5, 126.2* (3 *m*-Ph); 129.1, 129.17, 129.24 (3 *o*-Ph); 130.4, 130.9, 131.2 (3 *p*-Ph); 146.1 (C(5), ring B); 147.7 (C(3), ring A, ^3J = 4.3 Hz); 153.7 (C(5), ring A); 154.3 (br.s, C=O); 155.2 (C(3), ring C, ^3J = 3.7 Hz); 160.8 (C(3), ring B, ^3J = 4.4 Hz). MS, *m/z*: 447 $[M]^+$.

3-Chloro-1-[3-chloro-1-(3-chloro-1*H*-1,2,4-triazol-5-yl)-1,2,4-triazol-5-yl]-1*H*-1,2,4-triazol-5-one (11). A solution of NaOH (0.2 g) in water (0.5 mL) was added to a solution of TTT **7** (80 mg, 0.26 mmol) in DMF (0.5 mL). The reaction mixture was stirred for 15 min and poured into water with ice (20 g). The solution was neutralized with a concentrated aqueous HCl solution and extracted with EtOAc (2×20 mL). The extract was dried with $MgSO_4$. The solvent was distilled off *in vacuo*. The resulting oil was crystallized by adding a small amount of $CHCl_3$ and dried *in vacuo* at 80 °C over P_2O_5. Compound **11** was obtained in a yield of 52 mg (61%), m.p. 139—142 °C (from $CHCl_3$). Found (%): C, 22.59; H, 0.97; Cl, 32.59; N, 38.62. $C_6H_2Cl_3N_9O$. Calculated (%): C, 22.35; H, 0.63; Cl, 32.98; N, 39.09. IR (KBr), ν/cm^{-1}: 1779 (C=O). ^{1}H NMR (DMSO-d_6), δ: 14.45 (br.s, NH). ^{13}C NMR (DMSO-d_6), δ: 138.6, 143.5 (br), 145.1, 151.3 (br), 151.5, 152.0. MS, *m/z*: 321 $[M]^+$.

3-Chloro-1-[3-chloro-1-(3-chloro-1*H*-1,2,4-triazol-5-yl)-1,2,4-triazol-5-yl]-1*H*-1,2,4-triazol-5-ylamine (12). A solution of TTT **7** (100 mg, 0.33 mmol) in dry dioxane (2 mL) was saturated with dry ammonia at room temperature. After 3 h, saturation was repeated, and the reaction mixture was kept for 3 h. The precipitate that formed was filtered off and dried *in vacuo* at 80 °C. Compound **12** was obtained in a yield of 90 mg (83%), m.p. 223—224 °C. Found (%): C, 22.73; H, 1.37; Cl, 32.66; N, 43.42. $C_6H_3Cl_3N_{10}$. Calculated (%): C, 22.41; H, 0.94; Cl, 33.08; N, 43.57. ^{1}H NMR (DMSO-d_6), δ: 7.12 (br.s). ^{13}C NMR (DMSO-d_6), δ: 146.7, 147.5, 151.4, 153.0, 153.5, 158.0. MS, *m/z*: 320 $[M]^+$.

3,7,10-Triphenyltris[1,2,4]triazolo[1,5-*a*:4′,3′-*c*:4″,3″-*e*]-[1,3,5]triazine (13). Chlorotriazole **12** (80 mg, 0.17 mmol) was heated at 230—240 °C for 20 min. After cooling, the residue was extracted with hot acetone, and the solvent was distilled off *in vacuo*. Recrystallization of the residue from $CHCl_3$ afforded TTT **13** in a yield of 45 mg (71%) as colorless crystals, m.p. 331—334 °C (at this temperature, **13** was partially isomerized into TTT **14**). Found (%): C, 67.21; H, 3.50; N, 28.97. $C_{24}H_{15}N_9$. Calculated (%): C, 67.13; H, 3.52; N, 29.35. IR (KBr), ν/cm^{-1}: 694, 731, 1447, 1600. ^{1}H NMR (DMSO-d_6), δ: 7.58—7.62 (m, 3 H); 7.65—7.76 (m, 6 H); 8.05—8.11 (m, 6 H). MS, *m/z*: 429 $[M]^+$.

3,6,10-Triphenyltris[1,2,4]triazolo[1,5-*a*:1′,5′-*c*:4″,3″-*e*]-[1,3,5]triazine (14). ***A.*** Compound **2** was heated at 230 °C for 3 h. As a result, TTT **2** remained intact.

In an independent experiment, TTT **2** (100 mg, 0.23 mmol) was heated for 0.5 h with a gradual increase in the temperature from 330 to 360 °C. After cooling, the reaction mixture was extracted with hot acetone, and the solvent was distilled off *in vacuo*. The residue contained compound **14** and traces of compounds **1** and **13** (TLC). The chromatographic purification of the residue ($CHCl_3$—EtOAc, 2 : 1, as an eluent) afforded trimer **14** in a yield of 80 mg (80%) as colorless crystals, m.p. 307—310 °C (from acetone). Found (%): C, 67.32; H, 3.49; N, 29.18. $C_{24}H_{15}N_9$. Calculated (%): C, 67.13; H, 3.52; N, 29.35. IR (KBr), ν/cm^{-1}: 693, 727, 1447, 1620. ^{1}H NMR (DMSO-d_6), δ: 7.56—7.77 (m, 9 H); 8.08—8.18 (m, 4 H); 8.28—8.34 (m, 2 H). MS, *m/z*: 429 $[M]^+$.

B. Compound **13** (100 mg, 0.23 mmol) was heated at 330 °C for 40 min to prepare compound **14** in a yield of 98 mg (98%). The product is identical to that prepared according to the method ***A***.

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* Two superimposed signals.