Nitrogen-Rich Mesoionic Compounds from 1,3-Diaryl-5-chlorotetrazolium Salts and Nitrogen Nucleophiles − Synthesis and Properties of 1,3-Diaryl-5-azidotetrazolium Salts

Shuki Araki*, Kaori Yamamoto, Misako Yagi, Tomoko Inoue, Hiroyo Fukagawa, Hiromi Hattori, Hatsuo Yamamura, Masao Kawai, and Yasuo Butsugan

Department of Applied Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466, Japan
Fax: (internat.) + 81(0)52-735/5247
E-mail: araki@ach.nitech.ac.jp

Received June 16, 1997

Keywords: Azides / Betaines / Carbenes / Nitrogen heterocycles / Nucleophilic aromatic substitution

Nitrogen-rich mesoions have been synthesized by the reaction of the 5-chloro-1,3-diaryltetrazolium salt **1** with various nitrogen nucleophiles. The reactions with aqueous ammonia and hydroxylamine gave tripolar mesoionic amide **2** and mesoionic hydroxylamide **4**, respectively. *N*-Substituted and *N*,*N*-disubstituted hydrazines yielded the corresponding hydrazides **5**, whereas *N*,*N*-diphenylhydrazine gave the rearranged product **6**. The reaction with sodium azide gave 5-azidotetrazolium salt **8**. The azido group of **8** was reduced to give aminotetrazolium salt **9**, deprotonation of which yielded the corresponding conjugate base **3**. Hard nucleophiles attacked the tetrazolium carbon atom of **8** to give substitution products, whereas soft nucleophiles added the terminal nitrogen atom of the azido group to give addition products. Azidotetrazolium salt **8** reacted further with sodium azide to give a high yield of the tetrazol derivative **11**, together with a small amount of triazene **17**. The intermediacy of mesoionic carbene **19** is postulated.

Introduction

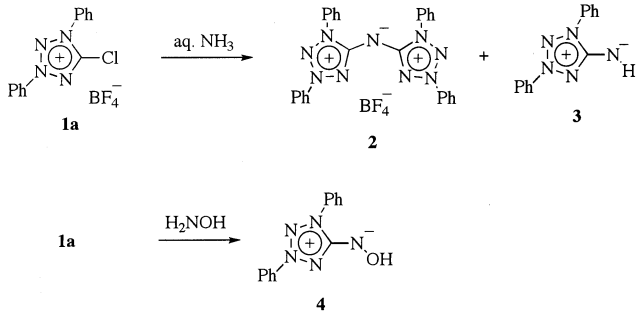
Polynitrogen as well as nitrogen-rich compounds are of special interest not only from a theoretical standpoint[1] but also owing to their practical importance such as high-energy materials of industrial and military use[2]. Although various types of nitrogen-rich compounds have been synthesized[3], mesoionic-type heterocycles are intriguing because of their unique electronic structures and interesting properties[4]. We have previously reported the synthesis of the 1,3-diaryl-5-chlorotetrazolium salt **1** and showed that it is a useful synthetic precursor to a variety of mesoionic systems; the chlorine atom of **1** is replaced readily by nucleophiles to give new mesoionic systems[5]. Therefore, it is expected that, on treatment with nitrogen nucleophiles, **1** gives mesoionic compounds with high nitrogen proportions. This paper describes the reactions of **1** with various nitrogen nucleophiles, including aqueous ammonia, hydroxylamine, and substituted hydrazines, which give several nitrogen-rich mesoionic amides. Furthermore, the reaction of **1** with sodium azide gives stable azidotetrazolium salts which show unique reaction behavior toward a variety of nucleophiles.

Results and Discussion

Reactions with Aqueous Ammonia, Hydroxylamine, and Hydrazines

The previously reported synthesis of compound **1**, by the action of chlorine on bis(diaryltetrazolio)mercury, requires relatively long synthetic procedures. We found that **1** can be synthesized in quantity simply by the chlorination of readily accessible 1,3-diaryltetrazolium-5-olate (**10**) with phosphoryl chloride. 5-Chloro-1,3-diphenyltetrazolium salt **1a** reacted smoothly with aqueous ammonia to give mesoionic bis(tetrazolio)amide **2** together with a small amount of tetrazolium-5-amide **3** (Scheme 1). Compound **2** is considered to be formed via **3**. Indeed, the reaction of **3** with **1a** gave a high yield of **2**. Although the yield of **3** is only modest, this compound can be prepared alternatively by the reduction of 5-azidotetrazolium salt (vide infra). We have recently reported the synthesis of the first tripolar mesoionic systems in which two tetrazolium rings share a common cyclopentadienide (or indenide) ring[6]. The amide **2** is a new member of such tripolar mesoions: two tetrazolium rings are connected with an exocyclic nitrogen atom. Treatment of **1a** with hydroxylamine gave reddish brown crystals of **4**. In this reaction, hydroxylamine reacted exclusively at the nitrogen atom.

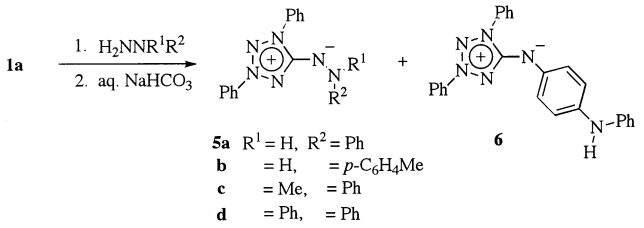
Scheme 1



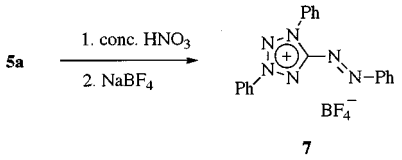
  1434−193X/98/0101−0121 $ 17.50+.50/0

Reaction of **1a** with *N*-substituted and *N,N*-disubstituted hydrazines gave the expected tetrazolium-5-hydrazides **5a**–**d**, after the treatment with a base (Scheme 2)[7]. Only in the case of *N,N*-diphenylhydrazine, a rearranged product **6** was obtained as the major product, together with a small amount of a normal substitution product **5d**. It was confirmed that the reaction of **1a** with 4-(phenylamino)phenylamine gives a high yield of **6**. Oxidation of phenylhydrazide **6a** with nitric acid gave an orange phenylazotetrazolium salt **7** (Scheme 3).

Scheme 2



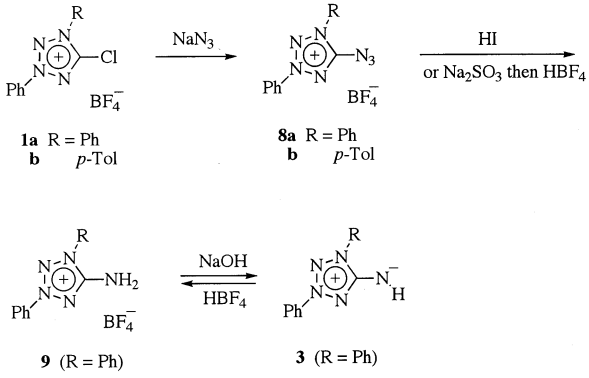
Scheme 3



Synthesis and Reactions of 1,3-Diaryl-5-azidotetrazolium Salt

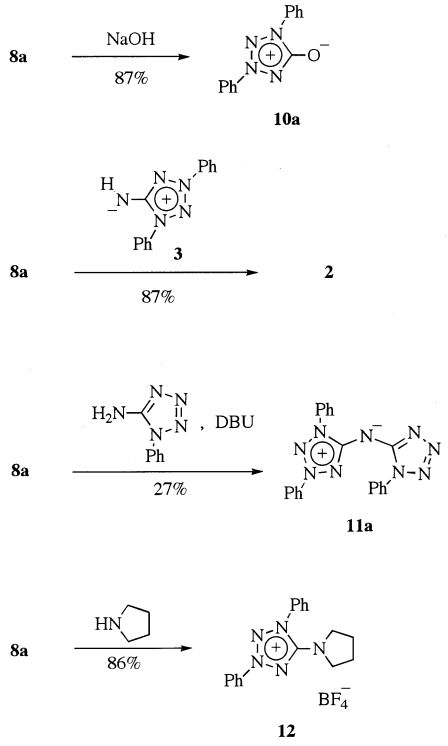
Chlorotetrazolium salt **1** reacted readily with an equimolar amount of sodium azide to give colorless crystals of azidotetrazolium salt **8** (Scheme 4). When excess sodium azide was employed, the yield of **8** dropped markedly and a new product **11** formed (vide infra). Azide **8** is stable at room temperature for several months without apparent decomposition. When heated, **8** decomposed nonexplosively at around 200°C to give a black tarry material. Crystals of **8** are impact-insensitive; no explosion was observed when struck by a hammer.

Scheme 4



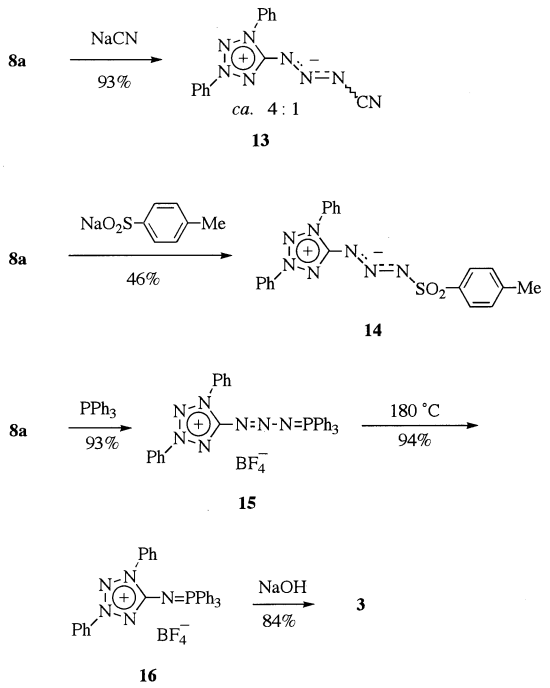
The azido group of azidotetrazolium salt **8a** was reduced readily by hydroiodic acid or sodium sulfite to gave aminotetrazolium salt **9.** Base treatment of **9** gave the corresponding conjugate base **3**, which was reversively protonated by tetrafluoroboric acid to give back **9**. Azidotetrazolium salt **8a** reacted with various nucleophiles. The results are summarized in Schemes 5 and 6. Hard nucleophiles, such as hydroxide ion and amines, attack at the tetrazolium carbon atom to give substitution products **10a**, **2**, **11a**, and **12**, whereas soft anions, such as cyanide and *p*-toluenesulfinate anions, attack at the terminal nitrogen atom of the azide group to give addition products **13** and **14**. Based on the ^{1}H- and ^{13}C-NMR spectra, **13** was a mixture of the geometrical isomers (ca. 4:1), whereas **14** was obtained as a sole isomer, presumably the *E* isomer. These reaction features of **8a** are very similar to those of Balli′s azidinium salts[8]. The reaction with triphenylphosphane, as a further example of soft bases, gave stable crystals of the 1:1 adduct **15**. The ^{13}C NMR shows complex signals suggesting that **15** exists as a mixture or in the equilibrium of possible geometrical isomers. Although the reaction of azides and triphenylphosphane is well known to give iminophosphoranes, the intermediate adducts have seldom been isolated and characterized so far[9]. Thermolysis of **15** at 180°C gave, with liberation of nitrogen, iminophosphorane **16**. Alkaline hydrolysis of **16** gave **3** and triphenylphosphane oxide. Each process from azidotetrazolium salt **8a** to tetrazolium amide **3** thus proceeded in good yield; therefore, this method provides an alternative synthetic route to aminotetrazolium salt **9**.

Scheme 5



In contrast to the corresponding 5-azido-2,3-diphenyltetrazolium salt[10], 5-azido-1,3-diphenyltetrazolium **8a** reacted readily with sodium azide to give high yields of tetrazol **11a** and phenyl azide, together with small amounts of triazene **17**, cyanotriazene **18**, and olate **10a** (Scheme 7). The compound **11a** is identical to the product from the re-

Scheme 6



action of **1a** and 5-amino-1-phenyltetrazol. A similar reaction of 5-azido-3-phenyl-1-*p*-tolyltetrazolium salt **8b** with sodium azide gave the corresponding di-*p*-tolyl derivative **11b** exclusively, and triphenyl compound **11a** was not formed at all in this reaction. Although the concrete mechanism for the formation of **11** is not unknown, a 1,3-diaryltetrazolylene **19** could be postulated as the key intermediate. Carbene species similar to **19** are known in the reaction of Balli's azidinium salts with azide, and triazene salts like **17** are reported to be the sole products via such carbene intermediates[11]. Cyanotriazene **18** is the ring-opening product of carbene **19a** as shown earlier[4]. Olate **10a** may be derived by the hydrolysis of **8a** or by the reaction of carbene **19a** with atmospheric oxygen; because nucleophilic carbenes such as 2,4-disubstituted triazolylene, a recently reported stable carbene, are reported to react readily with oxygen giving the corresponding olate[12].

We have previously described[5] that a mesoionic carbene **19** is generated by the deprotonation of the corresponding 1,3-diaryltetrazolium salt and can be trapped chemically with a 4-dimethylaminobenzenediazonium salt. However, carbene **19** is thermally unstable and undergoes a facile ring-opening to **18**. Similarly, the corresponding 2,3-diaryltetrazolylene is reported to give a ring-opening product[10]. The thermally labile feature of these mesoionic carbenes is in sharp contrast to the thermodynamic stability of Arduengo-type heterocyclic carbenes[13]. Further studies on the properties of the nitrogen-rich mesoionic compounds are now in progress.

This work was supported by a Grant-in-Aid for Scientific Research (No. 06640686) from the *Ministry of Education, Science, Sports and Culture*, Japan.

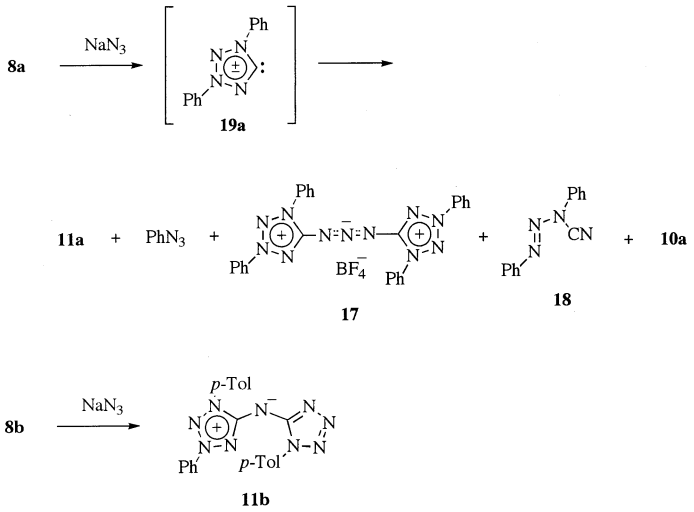
Experimental Section

General: Melting points (uncorrected): Hot-stage apparatus. − IR (KBr): JASCO A-102. − NMR: Varian XL-200, Varian Gemini 200 (200 MHz and 50 MHz, for ^{1}H and ^{13}C, respectively). ^{13}C-NMR data are summarized in Table 1. − UV/Vis: Hitachi 124, Hitachi U-3500. − MS (EI, 70 eV): Hitachi M-2000S. − Elemental analyses: Elemental Analysis Centre of Kyoto University. − ***Caution: Although we have never experienced explosions so far, the nitrogen-rich compounds synthesized in this work should be handled as potentially explosive materials!***

5-Chloro-1,3-diphenyltetrazolium Tetrafluoroborate (**1a**): 1,3-Diphenyltetrazolium-5-olate (**10a**, 5.0 g, 21 mmol) in phosphoryl chloride (11 ml) was heated at 90−100°C for 16 h. Excess phosphoryl chloride was removed under reduced pressure. The viscous oily residue was dissolved in aqueous tetrafluoroboric acid (42%, 22 ml) with ultrasonication for 30 min. The resulting white suspension was filtered, washed with a small amount of tetrahydrofuran, and dried under vacuum to give **2** (6.5 g, 90%). The product was identical to an authentic sample[5].

5-Chloro-3-phenyl-1-p-tolyltetrazolium Tetrafluoroborate (**1b**) was similarly prepared from 3-phenyl-1-*p*-tolyltetrazolium-5-olate[5]

Scheme 7



(**10b**, 1.2 g, 4.8 mmol) as a white powder (1.3 g, 75%). − M.p. 210°C (dec.; MeCN/Et_2O). − IR: $\tilde{\nu}$ = 1510 cm^{-1}, 1496, 1474, 1460, 1376, 1336, 1278, 1206, 1180, 1064, 824, 770, 684. − $C_{14}H_{12}BClF_4N_4$ (358.5): calcd. C 46.90, H 3.37, N 15.63; found C 46.11, H 3.22, N 15.47.

Reaction of **1a** *with Aqueous Ammonia:* To a suspension of **1a** (0.10 g, 0.29 mmol) in acetonitrile (5 ml), aqueous ammonia (28%, 0.50 ml, 7.4 mmol) was added, and the mixture was stirred at room temperature for 10 min. The solvent was removed under reduced pressure and the residue was column-chromatographed on alumina (CH_2Cl_2/acetone gradient) to give **10a** (3 mg) and a mixture of **2** and **3** (69 mg). The mixture of **2** and **3** was extracted with diethyl ether. Evaporation of the extracts gave **3** (8 mg, 12%). Compound **2** is insoluble in diethyl ether and obtained as the extraction residue (58 mg, 73%).

Bis(1,3-diphenyltetrazolio)amide Tetrafluoroborate (**2**): Colorless crystals. − M.p. 264−265°C (MeCN/Et_2O). − IR: $\tilde{\nu}$ = 1608 cm^{-1}, 1580, 1488, 1344, 1294, 1056, 982, 764, 678. − ^{1}H NMR ($CDCl_3$): δ = 7.59 (m, 6 H, *m* and *p* of Ph), 7.71 (m, 6 H, *m* and *p* of Ph), 8.05 (m, 4 H, *o* of Ph), 8.31 (m, 4 H, *o* of Ph). − UV/Vis (MeCN): λ_{max} (lg ε) = 276 nm (4.70), 346 (3.98). − $C_{26}H_{20}BF_4N_9$ (545.3): calcd. C 57.27, H 3.70, N 23.12; found C 57.26, H 3.77, N 23.34.

1,3-Diphenyltetrazolio-5-amide (**3**): Yellow crystals. − M.p. 115−117°C (hexane). − IR: $\tilde{\nu}$ = 3320 cm^{-1} (NH), 1618, 1590, 1484, 1374, 1334, 1244, 1182, 954, 754, 682. − ^{1}H NMR ($CDCl_3$): δ = 4.52 (br. s, 1 H, NH), 7.37 (br. t, *J* = 8 Hz, 1 H, *p* of Ph), 7.47−7.60 (m, 5 H, *m* and *p* of Ph), 8.08 (m, 2 H, *o* of Ph), 8.19 (br. d, *J* = 8 Hz, 2 H, *o* of Ph). − UV/Vis (MeCN): λ_{max} (lg ε) = 250 nm (4.14), 270 (sh, 4.02), 396 (3.54). − MS; *m/z* (%): 237 (100) [M^+], 105 (42) [PhN_2^+]. − $C_{13}H_{11}N_5$ (237.3): calcd. C 65.81, H 4.67, N 29.52; found C 65.90, H 4.92, N 29.52.

Reaction of **3** *with* **1a**: A mixture of **1a** (19 mg, 0.055 mmol) and **3** (13 mg, 0.055 mmol) in acetonitrile (3 ml) was stirred at room temperature for 10 min. The mixture was poured into aqueous sodium tetrafluoroborate and extracted with dichloromethane. The extracts were dried with anhydrous sodium sulfate and concentrated. The residue was recrystallized from ethanol to give **2** (13 mg, 87%). From the filtrate, aminotetrazolium **9** (8 mg) was obtained.

1,3-Diphenyltetrazolio-5-hydroxylamide (**4**): A mixture of hydroxylamine hydrochloride (0.63 g, 9.0 mmol) and triethylamine (1.3 ml, 9.0 mmol) in dry acetonitrile (30 ml) was stirred at room temperature for 1.5 h. To this mixture, **1a** (0.30 g, 0.87 mmol) was added in one portion and the mixture was vigorously stirred for 2 h. The solvent was evaporated under reduced pressure and the residue was partitioned between dichloromethane and water. The organic layer was separated, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica gel (CH_2Cl_2/acetone, 10 : 1) to give **10a** (45 mg, 22%), **2** (15 mg, 6%), and **4** (136 mg, 62%); **4** as reddish brown crystals. − M.p. 151−154°C (CH_2Cl_2/Et_2O). − IR: $\tilde{\nu}$ = 3330 cm^{-1}, 1640, 1592, 1502, 1490, 1460, 1382, 1328, 1300, 1214, 1172, 1070, 980, 920, 770, 748, 690. − ^{1}H NMR ($CDCl_3$): δ = 7.36 (t, *J* = 7 Hz, 1 H, *p* of Ph), 7.60 (m, 5 H, *m* and *p* of Ph), 8.06 (d, *J* = 8 Hz, 2 H, *o* of Ph), 8.19 (m, 2 H, *o* of Ph); in addition, a very broad signal centred at δ ≈ 4 was observed. − UV/Vis (MeCN): λ_{max} (lg ε) = 268 nm (4.29), 455 (3.51). − MS; *m/z* (%): 253 (15) [M^+], 118 (100). − $C_{13}H_{11}N_5O$ (253.3): calcd. C 61.65, H 4.38, N 27.65; found C 61.12, H 4.47, N 27.54.

1,3-Diphenyltetrazolio-5-phenylhydrazide (**5a**): A solution of **1a** (0.35 g, 1.0 mmol) and phenylhydrazine (0.54 g, 5.0 mmol) in dry acetonitrile (30 ml) was stirred for about 12 h at room temperature. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and shaked with saturated aqueous sodium hydrogen carbonate. The organic layer was separated, dried (Na_2SO_4), and passed through an alumina column to yield **5a** (0.22 g, 67%) as reddish purple crystals. − M.p. 127−130°C (acetone). − IR: $\tilde{\nu}$ = 3310 cm^{-1} (NH), 3060, 1636, 1590, 1488, 1330, 1212, 1162, 1050, 752, 686. − ^{1}H NMR ([D_6]DMSO): δ = 6.56 (t, *J* = 7 Hz, 1 H, *p* of N-Ph), 6.98 (d, *J* = 7 Hz, 2 H, *o* of N-Ph), 7.12 (t, *J* = 7 Hz, 2 H, *m* of N-Ph), 7.42 (t, *J* = 7 Hz, 1 H, Ph), 7.58−7.80 (m, 6 H, Ph and NH), 8.22 (m, 2 H, Ph), 8.35 (br. d, *J* = 8 Hz, 2 H, Ph). − UV/Vis (MeCN): λ_{max} (lg ε) = 280 nm (4.45), 495 (sh, 3.10), 517 (3.12). − MS; *m/z* (%): 328 (100) [M^+]. − $C_{19}H_{16}N_6$ (328.4): calcd. C 69.50, H 4.91, N 25.59; found C 69.72, H 5.05, N 25.44.

1,3-Diphenyltetrazolio-5-p-tolylhydrazide (**5b**): This compound was prepared in a similar manner as **5a** (0.24 g, 69%) to yield reddish purple crystals. − M.p. 160−163°C (acetone). − IR: $\tilde{\nu}$ = 3310 cm^{-1} (NH), 1642, 1610, 1590, 1572, 1508, 1490, 1464, 1380, 1332, 1298, 1258, 1220, 1184, 1164, 1120, 1066, 802, 750, 692, 684. − ^{1}H NMR ([D_6]DMSO): δ = 2.18 (s, 3 H, Me), 6.29 (m, 4 H, Ar-H), 7.44 (m, 1 H, *p* of Ph), 7.70 (m, 6 H, *m* and *p* of Ph, and NH), 8.22 (m, 2 H, *o* of Ph), 8.35 (m, 2 H, *o* of Ph). − UV/Vis (MeCN): λ_{max} (lg ε) = 279 nm (4.38), 355 (sh, 4.00), 394 (sh, 372), 499 (3.42), 526 (3.43). − MS; *m/z* (%): 342 (100) [M^+]. − $C_{20}H_{18}N_6$ (342.4): calcd. C 70.16, H 5.30; found C 69.92, H 5.25.

1,3-Diphenyltetrazolio-5-(N-methyl-N-phenylhydrazide) (**5c**): By a similar method as for **5a**, this compound was prepared from **1a** (0.35 g, 1.0 mmol) and *N*-methyl-*N*-phenylhydrazine (0.37 g, 3.0 mmol) to yield reddish purple crystals (0.13 g, 37%). − M.p. 145−148°C (diethyl ether/hexane). − IR: $\tilde{\nu}$ = 3060 cm^{-1}, 1610, 1585, 1487, 1328, 1290, 1100, 755, 690. − ^{1}H NMR ([D_6]DMSO): δ = 3.08 (s, 3 H, Me), 6.64 (t, *J* = 8 Hz, *p* of *N*-Ph), 6.95 (d, *J* = 8 Hz, 2 H, *o* of *N*-Ph), 7.13 (t, *J* = 8 Hz, 2 H, *m* of *N*-Ph), 7.45 (t, *J* = 8 Hz, 1 H, *p* of Ph), 7.65 (m, 5 H, *m* and *p* of Ph), 8.12 (m, 2 H, *o* of Ph), 8.35 (br. d, *J* = 8 Hz, 2 H, *o* of Ph). − UV/Vis (MeCN): λ_{max} (lg ε) = 268 nm (4.38). − MS; *m/z* (%): 342 (100) [M^+]. − $C_{20}H_{18}N_6$ (342.4): calcd. C 70.16, H 5.30, N 24.54; found C 70.38, H 5.42, N 24.61.

Reaction of **1a** *with N,N-Diphenylhydrazine:* A solution of **1a** (0.28 g, 0.80 mmol) and *N,N*-diphenylhydrazine (0.74 g, 4.0 mmol) in dry acetonitrile (30 ml) was stirred for about 12 h at room temperature. The solvent was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 and shaked with saturated aqueous sodium hydrogen carbonate. The organic layer was separated, dried (Na_2SO_4), and the residue was chromatographed on alumina (CH_2Cl_2) to yield **5d** (58 mg, 18%) and **6** (0.18 g, 57%).

1,3-Diphenyltetrazolio-5-(N,N-diphenylhydrazide) (**5d**): Reddish purple crystals. − M.p. 218°C (acetone). − IR: $\tilde{\nu}$ = 3070, 1620, 1585, 1490, 1330, 1295, 1170, 1070, 970, 750, 700 cm^{-1}. − ^{1}H NMR ([D_6]DMSO): δ = 6.87 (m, 2 H, *p* of N-Ph), 7.22 (m, 8 H, *o* and *m* of N-Ph), 7.49 (t, *J* = 8 Hz, 1 H, *p* of Ph), 7.65 (m, 5 H, *m* and *p* of Ph), 8.04 (m, 2 H, *o* of Ph), 8.37 (br. d, *J* = 8 Hz, 2 H, *o* of Ph). − UV/Vis (MeCN): λ_{max} (lg ε) = 260 nm (4.41), 304 (4.25), 395 (3.56). − MS; *m/z* (%): 404 (100) [M^+]. − $C_{25}H_{20}N_6$ (404.5): calcd. C 74.23, H 4.99, N 20.78; found C 74.52, H 4.79, N 20.89.

1,3-Diphenyltetrazolio-5-(p-N-phenylaminoanilide) (**6**): Reddish purple crystals. − M.p. 166−167°C (MeCN). − IR: $\tilde{\nu}$ = 3420 cm^{-1} (NH), 1628, 1615, 1585, 1495, 1330, 1313, 1287, 1275, 963, 762, 743, 690. − ^{1}H NMR ([D_6]DMSO): δ = 6.68 (t, *J* = 8 Hz, 1 H, *p* of N-Ph), 6.95 (d, *J* = 8 Hz, 2 H, *o* of N-Ph or ArH), 7.01 (d, *J* = 8 Hz, 2 H, *o* of N-Ph or ArH), 7.24 (t, *J* = 8 Hz, 2 H, *m* of N-Ph), 7.32 (d, *J* = 8 Hz, 2 H, ArH), 7.50 (d, *J* = 8 Hz, 1 H, *p* of

Ph), 7.66 (m, 5 H, *m* and *p* of Ph), 7.82 (s, 1 H, NH), 8.20 (m, 2 H, *o* of Ph), 8.35 (br. d, J = 8 Hz, 2 H, *o* of Ph). − UV/Vis (MeCN): λ_{max} (lg ε) = 263 nm (sh, 4.36), 317 (4.54), 458 (3.51). − MS; *m/z* (%): 404 (100) [M^+]. − $C_{25}H_{20}N_6$ (404.5): calcd. C 74.23, H 4.99, N 20.78; found C 74.38, H 5.17, N 20.96. − This compound **6** was alternatively prepared by the reaction of **1a** with 4-(aminophenyl)phenylamine: **1a** (0.35 g, 1.0 mmol) and 4-(aminophenyl)phenylamine (0.37 g, 2.0 mmol) were stirred for about 12 h in acetonitrile (18 ml) at room temperature. The mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane and shaked with saturated aqueous sodium hydrogen carbonate. The organic layer was separated, dried (Na_2SO_4), and concentrated. The residue was chromatographed on alumina (CH_2Cl_2) to yield **6** (0.29 g, 72%).

1,3-Diphenyl-5-phenylazotetrazolium Tetrafluoroborate (**7**): Crystals of phenylhydrazide **5a** (66 mg, 0.20 mmol) were added to conc. nitric acid (0.5 ml) and the mixture was stirred at room temperature for 3 min. Aqueous sodium tetrafluoroborate was added, and the product was extracted with dichloromethane. The extracts were dried with anhydrous sodium sulfate, and the solvent was removed. The residue was recrystallized from MeCN/diethyl ether to give **7** (65 mg, 78%) as orange crystals. − M.p. 180−182°C. − IR: $\tilde{\nu}$ = 1596 cm^{-1}, 1492, 1420, 1200, 1148, 1082, 1060, 782, 764, 680. − ^{1}H NMR (CF_3COOD): δ = 7.72 (t, J = 8 Hz, 2 H, *m* of N=N−Ph), 7.78-8.00 (m, 7 H, *m* and *p* of Ph, *and p* of N=N−Ph), 8.08 (d, J = 8 Hz, 2 H, *o* of N=N−Ph), 8.23 (d, J = 8 Hz, 2 H, *o* of Ph), 8.48 (d, J = 8 Hz, 2 H, *o* of Ph). − UV/Vis (MeCN): λ_{max} (lg ε) = 332 nm (4.40), 466 (sh, 3.21). − $C_{19}H_{15}BF_4N_6$ (414.2): calcd. C 55.10, H 3.65; found C 55.37, H 3.49.

5-Azido-1,3-diphenyltetrazolium Tetrafluoroborate (**8a**): To a suspension of **1a** (0.69 g, 2.0 mmol) in DMF (2 ml) was added a powder of sodium azide (0.13 g, 2.0 mmol) at 0°C, and the mixture was stirred for about 12 h at room temperature. Water was added and the resulted precipitate was filtered, washed with water, and dried yielding a pale yellow powder of crude **8a** (0.60 g, 86%). This crude product was recrystallized from EtOH (80 ml) to give pure **8a** (0.44 g, 63%) as colorless crystals. − M.p. 209−211°C (dec.). − IR: $\tilde{\nu}$ = 2180 cm^{-1} (N_3), 1596, 1550, 1486, 1464, 1378, 1340, 1296, 1272, 1230, 1082, 1060, 766, 680. − ^{1}H NMR ([D_6]DMSO): δ = 7.80−8.00 (m, 8 H, Ph), 8.35 (m, 2 H, *o* of Ph). − $C_{13}H_{10}BF_4N_7$ (351.1): calcd. C 44.48, H 2.87, N 27.92; found C 44.55, H 2.65, N 27.78.

5-Azido-3-phenyl-1-p-tolyltetrazolium Tetrafluoroborate (**8b**) was similarly prepared from **1b** (0.36 g, 1.0 mmol) to yield as colorless crystals (0.23 g, 63%). − M.p. 188−190°C (dec., EtOH). − IR: $\tilde{\nu}$ = 2200 cm^{-1} (N_3), 1598, 1550, 1508, 1464, 1374, 1342, 1296, 1270, 1228, 1186, 1160, 1060, 816, 764, 680. − ^{1}H NMR ([D_6]DMSO): δ = 2.49 (s, 3 H, Me), 7.64 (d, J = 8 Hz, 2 H, Ar), 7.79−7.98 (m, 5 H, Ar and Ph), 8.27−8.42 (m, 2 H, *o* of Ph). − $C_{14}H_{12}BF_4N_7$ (365.1): calcd. C 46.06, H 3.31, N 26.85; found C 46.17, H 3.22, N 27.04.

Reduction of **8a** *with Hydrogen Iodide:* To a solution of **8a** (1.0 g, 3.0 mmol) in acetonitrile (30 ml) was added aqueous hydrogen iodide (55%; 2 ml, 15 mmol) at −40°C and the mixture was gradually warmed to room temperature. The solvent was removed under reduced pressure, and tetrafluoroboric acid (10%; 5 ml) and diethyl ether (100 ml) were added to the residue. The precipitate was filtered, washed with water, and recrystallized from ethanol to give 5-amino-1,3-diphenyltetrazolium tetrafluoroborate (**9**) (0.50 g, 51%). − M.p. 195°C (EtOH). − IR: $\tilde{\nu}$ = 3430 cm^{-1}, 3050, 1640, 1492, 1202, 1082, 1032, 756, 684. − ^{1}H NMR ([D_6]DMSO): δ = 7.72−7.90 (m, 8 H, Ph), 8.16 (m, 2 H, *o* of Ph), 8.67 (br. s, 2 H, NH_2). − $C_{13}H_{12}BF_4N_5$ (325.1): calcd. C 48.03, H 3.72, N 21.54; found C 47.99, H 3.86, N 21.54.

Reduction of **8a** *with Sodium Sulfite:* To a solution of **8a** (40 mg, 0.11 mmol) in DMSO (1 ml) was added sodium sulfite (20 mg, 0.16 mmol) in water (2 ml) at room temperature. Nitrogen was evolved vigorously and a yellow solution was obtained. After 10 min, saturated aqueous sodium hydrogen carbonate was added and the product was extracted several times with dichloromethane. The solvent was evaporated and the residue was dissolved in ethanol (1 ml), which was acidified by the addition of a few drops of tetrafluoroboric acid (42%) and then diethyl ether was added. The resulting crystals were filtered and recrystallized from ethanol/diethyl ether to give **9** (24 mg, 65%).

1,3-Diphenyltetrazolio-5-amide (**3**): A solution of **9** (53 mg, 0.16 mmol) in dichloromethane (5 ml) was shaked with aqueous sodium hydroxide (1 N, 5 ml). An intense yellow color immediately developed. The organic layer was separated, dried with anhydrous sodium sulfate, and concentrated. The residue was recrystallized from hexane to give **3** (39 mg, 100%).

Alkaline Hydrolysis of **8a**: To a solution of **8a** (22 mg, 0.063 mmol) in DMF (0.5 ml) was added 10 drops of aqueous sodium hydroxide (1 N) and the mixture was stirred for 1 h. The mixture was poured into water and the product was extracted with dichloromethane. The extracts were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (silica gel/dichloromethane) to give **10a** (13 mg, 87%).

Reaction of **8a** *with* **3**: A mixture of **8a** (33 mg, 0.094 mmol) and **3** (50 mg, 0.21 mmol) in acetonitrile (1 ml) was stirred at room temperature for 10 min. One drop of aqueous tetrafluoroboric acid (50%) was added and the solvent was evaporated. The residue was recrystallized from ethanol to give **2** (44 mg, 87%). From the filtrate, **9** (31 mg, 82%) was obtained.

1,3-Diphenyltetrazolio-5-(1-phenyltetrazol-5-yl)amide (**11a**): DBU (50 µl, 0.33 mmol) was added to a mixture of **8a** (44 mg, 0.13 mmol) and 5-amino-1-phenyltetrazol[14] (23 mg, 0.14 mmol) in dichloromethane (2 ml). The mixture was stirred at room temperature for 13 h. The solvent was evaporated and the residue was chromatographed on silica gel (CH_2Cl_2) to give **11a** (13 mg, 27%) and olate **10a** (13 mg, 43%). A similar reaction of **1a** (35 mg, 0.10 mmol) and 5-amino-1-phenyltetrazol (20 mg, 0.12 mmol) in dichloromethane (2 ml) gave **11a** (17 mg, 45%) and olate **10a** (6 mg, 25%). This compound **11a** was alternatively prepared by the reaction of **8a** with sodium azide (vide infra). **11a**: Yellow crystals. − M.p. 227−228°C (benzene). − IR: $\tilde{\nu}$ = 1604 cm^{-1}, 1574, 1520, 1492, 1388, 1092, 968, 762, 750, 678. − ^{1}H NMR ($CDCl_3$): δ = 7.34−7.68 (m, 9 H, Ph), 7.96 (m, 2 H, *o* of Ph), 8.15 (m, 2 H, *o* of Ph), 8.31 (m, 2 H, *o* of Ph). − UV/Vis (MeCN): λ_{max} (lg ε) = 236 nm (sh, 4.16), 286 (4.49), 373 (3.47). − MS; *m/z* (%): 381 (23) [M^+], 248 (100) [M^+ − PhN_4]. − $C_{20}H_{15}N_9$ (381.4): calcd. C 62.98, H 3.96, N 33.05; found C 62.90, H 4.09, N 33.00.

1,3-Diphenyl-5-pyrrolidyltetrazolium Tetrafluoroborate (**12**): To a solution of **8a** (35 mg, 0.10 mmol) in dichloromethane (3 ml) were added a few drops of pyrrolidine (gas evolution). The mixture was stirred for 10 min and water was added. The dichloromethane layer was separated, dried (Na_2SO_4), and concentrated. The residue was recrystallized from ethanol to give **12** (32 mg, 86%): colorless crystals. − M.p. 192−193°C. − IR: $\tilde{\nu}$ = 2990 cm^{-1}, 2890, 1640, 1590, 1492, 1458, 1380, 1354, 1300, 1282, 1206, 1154, 962, 766, 718, 698, 682, 672. − ^{1}H NMR ($CDCl_3$): δ = 1.92 (m, 4 H, CH_2), 3.39 (m, 4 H, CH_2), 7.60 (m, 6 H, *m* and *p* of Ph), 7.86 (d, J = 8 Hz, 2 H, *o* of Ph), 8.09 (d, J = 8 Hz, 2 H, *o* of Ph). − $C_{17}H_{18}BF_4N_5$ (379.2): calcd. C 53.85, H 4.78, N 18.47; found C 54.13, H 4.82, N 18.58.

Table 1. ^{13}C-NMR data for new compounds

Compound	Solvent	Phenyl group on tetrazolium ring				C^+	Others
		C_{ortho}	C_{meta}	C_{para}	C_{ipso}		
2	$[D_6]$DMSO	121.0, 124.5	129.7, 130.8	131.1, 132.9	132.7, 135.7	156.9	
3	$CDCl_3$	120.2, 121.0	129.5, 129.8	127.8, 131.3	135.5, 136.3	162.1	
4	$CDCl_3$	119.8, 120.2	129.2, 129.4	127.3, 131.3	134.8, 135.8	159.8	
5a	$[D_6]$DMSO	119.1, 120.5	129.5, 130.1	127.1, 131.8	135.3, 136.0	153.7	112.1 (NPh, *o*), 116.3 (NPh, *p*), 128.7 (NPh, *m*), 149.1 (NPh, *i*)
5c	$CDCl_3$	120.9, 121.2	129.0[a], 130.0[a]	128.1, 131.8	135.9, 136.7	162.3	41.0 (NMe), 114.7 (NPh, *o*), 118.3 (NPh, *p*), 129.8 (NPh, *m*)[a], 153.0 (NPh, *i*)
5d	$[D_6]$DMSO	120.4[a], 120.8[a]	129.5, 130.1	128.1, 131.8	135.0, 135.7	163.5	119.4 (NPh, *o*), 121.1 (NPh, *p*)[a], 128.7 (NPh, *m*), 148.2 (NPh, *i*)
6	$[D_6]$DMSO	119.4[a], 120.4[a]	129.1[b], 129.2[b]	128.1, 131.6	135.0[c], 135.6[c]	153.6	114.8 (NPh, *o*), 118.0 (NPh, *p*), 121.6 (ArCH)[a], 123.1 (ArCH)[a], 130.1 (NPh, *m*)[b], 136.0 (ArCH)[c], 142.7 (ArCH)[c], 145.3 (NPh, *i*)[c]
7	CF_3COOD	123.1[a], 127.1[a]	132.3[b], 132.6[b]	135.7, 136.8	133.7, 137.4	162.6	128.1 (NPh, *o*)[a], 132.8 (NPh, *m*)[b], 140.8 (NPh, *p*), 155.9 (NPh, *i*)
8a	$[D_6]$DMSO	121.3, 124.7	130.7, 131.2	133.1, 134.3	130.5, 134.7	155.9	
8b	$[D_6]$DMSO	121.3[a]	130.9[b]	134.2	128.0[c]	155.8	21.1 (Me), 124.4 (*o* of Tol)[a], 131.1 (*m* of Tol)[b], 134.7 (*i* of Tol)[c], 143.6 (*p* of Tol)
9	$[D_6]$DMSO	120.9, 126.0	130.6, 130.8	132.3, 133.1	130.8, 135.1	157.7	
11a	$CDCl_3$	120.9[a], 123.0[a]	129.0[b], 129.6[b]	128.0[c], 130.0[c]	134.0[d], 135.7[d]	157.4	123.2 (NPh, *o*)[a], 130.2 (NPh, *m*)[b], 132.5 (NPh, *p*)[c], 136.0 (NPh, *i*)[d], 156.0 (tetrazol C)
12	$CDCl_3$	121.6, 128.2	130.0, 130.2	132.6, 133.1	132.4, 135.6	156.3	25.7 (CH_2), 50.5 (CH_2)
13[e]	$[D_6]$DMSO	121.1, 125.3	129.8, 130.6	131.5, 133.1	135.3, 135.3	162.8	119.9 (CN)
14	$[D_6]$DMSO	121.0, 125.1	129.6[a], 129.7[a]	131.2, 132.9	132.5[b], 135.4[b]	163.9	21.1 (Me), 128.1 (ArCH)[a], 130.6 (ArCH)[a], 136.4 (Ar*C*−Me)[b], 143.4 (ArC−SO_2)
16	$CDCl_3$	120.7, 123.9	130.0, 130.3	131.1, 132.7	132.5, 135.5	157.7	124.7 ($J_{C\text{-}P}$ = 103 Hz, PPh_3, *i*), 129.8($J_{C\text{-}P}$ = 13 Hz, PPh_3, *m*), 133.1 ($J_{C\text{-}P}$ = 11 Hz, PPh_3, *o*), 129.2 ($J_{C\text{-}P}$ = 4 Hz, PPh_3, *p*)
17	$[D_6]$DMSO	121.2, 125.6	130.0, 130.9	131.9, 133.3	132.3, 135.4	163.0	

[a]−[d] The individual-letter values may be interchanged. − [e] For the major isomer.

1,3-Diphenyltetrazolio-5-(3-cyanotriazide) (**13**): A mixture of **8a** (70 mg, 0.20 mmol) and sodium cyanide (15 mg, 0.30 mmol) in DMF (0.5 ml) was ultrasonicated for 3 h. Water was added to a reaction mixture and the resulting precipitate was filtered. Recrystallization from acetonitrile gave pale yellow crystals of **13** (54 mg, 93%) as a mixture of geometrical isomers (ca. 4:1). − M.p. 216−218°C. − IR: $\tilde{\nu}$ = 2170 cm^{-1} (CN), 1508, 1456, 1242, 1212, 1168, 1074, 760, 700, 674. − ^{1}H NMR ($[D_6]$DMSO): δ = 7.68−7.85 (m, 6 H, *m* and *p* of Ph), 7.95 (m, 1.6 H, *o* of Ph), 8.06 (m, 0.4 H, *o* of Ph), 8.29 (m, 2 H, *o* of Ph). − UV/Vis (DMSO): λ_{max} (lg ε) = 274 nm (sh, 4.06), 330 (4.39). − MS; *m/z* (%): 290 (0.9) [M^+], 77 (100) [Ph]. − $C_{14}H_{10}N_8$ (290.3): calcd. C 57.93, H 3.47, N 38.60; found C 57.99, H 3.25, N 38.45.

1,3-Diphenyltetrazolio-5-[3-(p-toluenesulfonyl)triazide] (**14**): A mixture of **8a** (70 mg, 0.20 mmol) and sodium *p*-toluenesulfinate (75 mg, 0.30 mmol) in DMF (1 ml) was stirred at room temperature for 3 h. Water was added and the resulted precipitate was filtered and recrystallized from ethanol to give **14** (39 mg, 46%) as pale yellow crystals. − M.p. 143−144°C. − IR: $\tilde{\nu}$ = 3080 cm^{-1}, 1596, 1522, 1486, 1460, 1414, 1378, 1318, 1290, 1256, 1174, 1144, 1082, 990, 940, 818, 760, 672. − ^{1}H NMR ($[D_6]$DMSO): δ = 2.38 (s, 3 H, Me), 7.40 (d, *J* = 8 Hz, 2 H, Ar), 7.66−7.84 (m, 8 H, *m* and *p* of Ph, and Ar), 7.92 (m, 2 H, *o* of Ph), 8.20 (m, 2 H, *o* of Ph). − UV/Vis (DMSO): λ_{max} (lg ε) = 321 nm (4.29). − MS; *m/z* (%): 391 (100) [$M^+ - N_2$], 327 (47) [$M^+ - N_2 - SO_2$]. − $C_{20}H_{17}N_7O_2S$ (419.5): calcd. C 57.26, H 4.09, N 23.38; found C 57.00, H 4.11, N 23.34.

1,3-Diphenyl-5-(triphenylphosphonotriazo)tetrazolium Tetrafluoroborate (**15**): To a suspension of **8a** (0.18 g, 0.50 mmol) in dichloromethane (5 ml) was added triphenylphosphane (131 mg, 0.50 mmol). The mixture turned immediately to yellow. The mixture was allowed to stand at room temperature for 15 min. The solvent was evaporated and the residue was recrystallized from dichloromethane/diethyl ether to give **15** (0.29 g, 93%) as pale yellow crystals. − M.p. 155°C (dec.). − IR: $\tilde{\nu}$ = 1520 cm^{-1}, 1434, 1280, 1252, 1080, 1052, 994, 760, 718, 696, 678. − ^{1}H NMR ($CDCl_3$): δ = 7.50−7.83 (m, 24 H, Ph), 8.05 (m, 2 H, *o* of Ph), 8.20 (m, 2 H, *o* of Ph). − $C_{31}H_{25}BF_4N_7P$ (613.4): calcd. C 60.70, H 4.11, N 15.99; found C 60.33, H 4.06, N 15.95.

1,3-Diphenyl-5-(triphenylphosphonoimino)tetrazolium Tetrafluoroborate (**16**): Crystals of **15** (50 mg, 0.082 mmol) were gradually heated under vacuum (ca. 5 Torr). At ca. 150−160°C, decomposition started suddenly with the vigorous evolution of nitrogen. The pyrolysis was continued at 180°C for 30 min. After being cooled to room temperature, the pyrolysate was recrystallized from acetonitrile/diethyl ether to give **16** (45 mg, 94%) as colorless crystals. − M.p. 223−224°C. − IR: $\tilde{\nu}$ = 1600 cm^{-1}, 1580, 1562, 1484, 1434, 1338, 1112, 1080, 1048, 968, 764, 720, 688. − ^{1}H NMR ($CDCl_3$): δ = 7.54−7.73 (m, 15 H, PPh_3), 7.73−7.92 (m, 8 H, Ph), 8.17 (m, 2 H, *o* of Ph). − UV/Vis (MeCN): λ_{max} (lg ε) = 225 nm (4.46), 255 (4.24), 267 (sh, 4.17), 274 (sh, 4.09), 323 (3.84). − $C_{31}H_{25}BF_4N_5P$ (585.3): calcd. C 63.61, H 4.31, N 11.98; found C 63.48, H 4.30, N 12.00.

Hydrolysis of **16**: Into a solution of compound **16** (50 mg, 0.082 mmol) in DMSO (1 ml) was added aqueous sodium hydroxide (0.5 N, 0.2 ml, 0.10 mmol), and a mixture was allowed to stand for 5 min. After the reaction mixture was acidified to pH = 1 with diluted aqueous tetrafluoroboric acid, the mixture was extracted with dichloromethane. The extract was washed with water, dried (Na_2SO_4), and concentrated to leave triphenylphosphane oxide (18 mg, 78%). The aqueous layer was made alkaline (pH = 14) with sodium hydroxide and extracted with dichloromethane. From the extracts, yellow crystals of **3** (16 mg, 84%) were obtained.

Reaction of **8a** *with Sodium Azide:* Sodium azide (26 mg, 0.40 mmol) was added to **8a** (70 mg, 0.20 mmol) in DMF (0.5 ml) at

room temperature. An exothermic reaction occurred immediately (gas evolution) and the mixture turned to yellow. The mixture was stirred at room temperature for 12 h. Water was added and the resulting yellow precipitate was filtered. The filtrate was analyzed by ^{1}H-NMR spectroscopy to reveal that phenyl azide formed quantitatively. The yellow precipitate was chromatographed on silica gel (CH_2Cl_2) to give **11a** (33 mg, 87%) and a trace amount (ca. 1−2 mg) of **17**. The product **11a** was identical with the compound obtained from the reaction of **1a** and 5-amino-1-phenyltetrazol. When the same reaction of **8a** (0.42 g, 1.2 mmol) and sodium azide (78 mg, 1.2 mmol) in DMF (3 ml) was done at −50°C for 3 h and then at room temperature for 20 h, the following products were isolated: **11a** (51%), **18** (12%), **17** (7%), and **10a** (4%).

5-[3-(1,3-Diphenyl-5-tetrazolylene)-1-triazeno]-1,3-diphenyltetrazolium Tetrafluoroborate (**17**): Yellow crystals. − M.p. 242−243°C (dec.; EtOH). − IR: $\tilde{\nu}$ = 1492 cm^{-1}, 1260, 1242, 1194, 1080, 1054, 756. − ^{1}H NMR ([D$_6$]DMSO): δ = 7.77 (m, 6 H, *m* and *p* of Ph), 7.85 (m, 6 H, *m* and *p* of Ph), 7.96 (m, 2 H, *o* of Ph), 8.31 (m, 2 H, *o* of Ph). − UV/Vis (DMSO): λ_{max} (lg ε) = 278 nm (4.16), 358 (4.27). − $C_{26}H_{20}BF_4N_{11}$ (573.3): calcd. C 54.47, H 3.52, N 26.87; found C 54.61, H 3.39, N 26.55.

3-Phenyl-1-p-tolyl-5-(1-p-tolyltetrazol-5-yl)amide (**11b**) was similarly obtained in almost quantitative yield from the reaction of 5-azido-3-phenyl-1-*p*-tolyltetrazolium tetrafluoroborate (**8b**) (0.23 g, 0.60 mmol) and sodium azide (78 mg, 1.2 mmol) in DMF (1.5 ml) at room temperature as yellow crystals. − M.p. 273−276°C (dec.; EtOH/acetone). − IR: $\tilde{\nu}$ = 1614 cm^{-1}, 1596, 1576, 1508, 1364, 1334, 1284, 1174, 1098, 972, 810, 774. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.39 (s, 3 H, Me), 2.44 (s, 3 H, Me), 7.35 (d, *J* = 8 Hz, 2 H, Ar), 7.47 (d, *J* = 8 Hz, 2 H, Ar), 7.76 (m, 5 H, Ar and Ph), 7.99 (d, *J* = 8 Hz, 2 H, Ar), 8.21 (m, 2 H, *o* of Ph). − UV/Vis (MeCN): λ_{max} (lg ε) = 237 nm (4.02), 284 (4.29), 378 (3.32). − MS; *m/z* (%): 490 (8) [M$^+$], 262 (100) [M$^+$ − TolN$_4$]. − $C_{22}H_{19}N_9$ (409.5): calcd. C 64.54, H 4.68, N 30.79; found C 64.55, H 4.84, N 30.50.

[1] M. N. Glukhovtsev, H. Jiao, P. von Rague Schleyer, *Inorg. Chem.* **1996**, *35*, 7124−7133, and references cited therein.

[2] F. R. Benson, *The High Nitrogen Compounds,* John Wiley, New York, **1984**, pp. 6−263.

[3] For a recent example: see: G. Subramanian, G. Eck, J. H. Boyer, E. D. Stevens, M. L. Trudell, *J. Org. Chem.*, **1996**, *61*, 5801−5803.

[4] [4a] M. Ohta, H. Kato, *Nonbenzenoid Aromatics* (Ed.: J. P. Snyder), Academic Press, New York, **1969**, pp. 117−248. − [4b] W. D. Ollis, C. A. Ramsden, *Adv. Heterocycl. Chem.* **1976**, *19*, 1−122. − [4c] C. G. Newton, C. A. Ramsden, *Tetrahedron* **1982**, *38*, 2965−3011.

[5] S. Araki, Y. Wanibe, F. Uno, A. Morikawa, K. Yamamoto, K. Chiba, Y. Butsugan, *Chem. Ber.* **1993**, *126*, 1149−1155.

[6] S. Araki, J. Mizuya, N. Aoyama, Y. Butsugan, *J. Chem Soc., Perkin Trans. 1* **1995**, 1989−1991.

[7] The reaction of **1** with hydrazine hydrate gave the corresponding mesoionic azine. The results will be reported elsewhere.

[8] [8a] H. Balli, *Justus Liebigs Ann. Chem.* **1961**, *647*, 11−18. − [8b] H. Balli, B. Hellrung, A. Kneubühler-Hof, *Helv. Chim. Acta* **1974**, *57*, 1178−1185. − [8c] B. Hellrung, H. Balli, *Helv. Chim. Acta* **1974**, *57*, 1185−1191. − [8d] H. Balli, *Helv. Chim. Acta* **1974**, *57*, 1912−1919. − [8e] B. Hellrung, H. Balli, *Helv. Chim. Acta* **1975**, *58*, 596−604. − [8f] B. Hellrung, H. Balli, *Helv. Chim. Acta* **1976**, *59*, 140−148.

[9] For example: [9a] J. E. Leffler, U. Honsberg, Y. Tsuno, I. Forsblad, *J. Org. Chem.* **1961**, *26*, 4810−4814. − [9b] P. Laszlo, E. Polla, *Tetrahedron Lett.* **1984**, *25*, 4651−4654. − See also ref.[8d].

[10] [10a] R. Weiss, R. H. Lowack, *Angew. Chem.* **1991**, *103*, 1183−1184; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1162−1163. − [10b] R. H. Lowack, R. Weiss, *J. Am. Chem. Soc.* **1990**, *112*, 333−338.

[11] [11a] H. Balli, F. Kersting, *Justus Liebigs Ann. Chem.* **1963**, *663*, 96−103. − [11b] H. Balli, F. Kersting, *Justus Liebigs Ann. Chem.* **1963**, *663*, 103−107. − [11c] D. Schelz, H. Balli, *Helv. Chim. Acta* **1970**, *53*, 1913−1917. − [11d] H. Balli, R. Maul, *Helv. Chim. Acta* **1976**, *59*, 148−155. − [11e] H. Balli, R. Löw, *Helv. Chim. Acta* **1976**, *59*, 155−164.

[12] D. Enders, K. Breuer, J. Runsink, J. H. Teles, *Liebigs Ann.* **1996**, 2019−2028.

[13] [13a] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361−363. − [13b] A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530−5534. − [13c] A. J. Arduengo III, J. R. Goerlich, W. J. Marshall, *J. Am. Chem. Soc.* **1995**, *117*, 11027−11028. − [13d] A. J. Arduengo III, J. R. Goerlich, W. J. Marshall, *Liebigs Ann.* **1997**, 365−374. − See also: [13e] M. Regitz, *Angew. Chem.* **1996**, *108*, 791−794; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 725−728, and references cited therein.

[14] W. G. Finnegan, R. A. Henry, E. Lieber, *J. Org. Chem.* **1953**, *18*, 779−791.

[97178]