Synthesis and Chemical Transformations of 1,3-Diaryltetrazolium Salts. Preparation of Mercury(II) and Palladium(II) Complexes of 1,3-Diaryltetrazolylene and Reactions of 5-Substituted 1,3-Diphenyltetrazolium Salts with Nucleophiles

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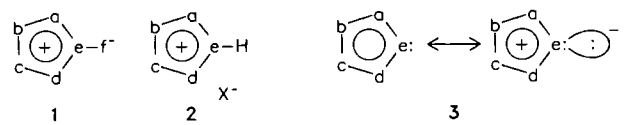
1,3-Diaryltetrazolium salts **5** and **6** have been prepared by nitric acid oxidation of the corresponding 5-thiolates **4**. The reaction of **5** with mercury(II) acetate gives (1,3-diaryltetrazolylene)mercury(II) complexes **7**, which provide 5-halotetrazolium salts **8**–**10** by treatment with halogen. 1,3-Diphenyltetrazolylene (**16**), generated in situ by proton abstraction of 1,3-diphenyltetrazolium salts **5a** or **6a**, has been trapped with *p*-(dimethylamino)benzenediazonium tetrafluoroborate to form **18**/**18′**. The palladium(II) complex **19** of 1,3-diphenyltetrazolylene has been prepared by oxidative addition of tetrakis(triphenylphosphane)palladium(0) to 5-chlorotetrazolium salt **8**. The reactivity of various 5-substituted tetrazolium salts toward carbon nucleophiles depends on the nature of the substituents at C-5. With electronegative substituents, nucleophilic substitution proceeds at C-5, whereas electron-donating substituents direct the nucleophiles towards N-2 yielding ring-cleaved products.

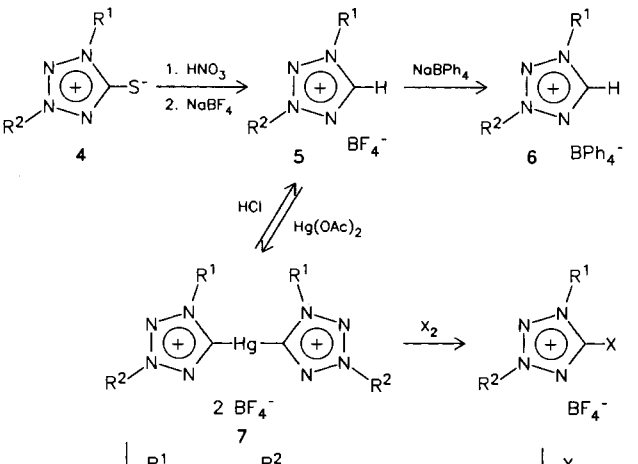
Mesoionic compounds of type **1** are an interesting family of heterocycles because of their unique structure, reaction behaviour, and biological activities. A number of mesoionic compounds have hitherto been prepared and extensively studied[1]. Heterocyclic cations **2** derived from **1**, where its exocyclic anionic group (f^-) has been replaced by hydrogen, are expected to be of synthetic value as precursors to mesoionic systems with different exocyclic groups. Cations **2** are also interesting as the conjugate acids of heterocyclic carbenes **3**. The latter are particularly intriguing molecules, since an aromatic canonical form is expected to contribute to its ground-state electronic structure, and hence compounds **3** are expected to behave as aromatic carbenes. As an example of such mesoionic carbenes, Weiss has recently reported on the generation of 2,3-diaryltetrazolylenes by deprotonation of the corresponding tetrazolium salts and has discussed their properties[2]. As a part of our work on mesoionic tetrazolium compounds[3], we describe in this paper the preparation of 1,3-diaryltetrazolium salts and their transformations to various 5-substituted derivatives. 1,3-Diaryltetrazolium mesoionic compounds belong to type A mesoions, whereas Weiss's 2,3-diaryl isomers are examples of type B mesoionic compounds[1].



1 2 3

Synthesis

When mesoionic thiolates[2a] and selenolates[4] are dissolved in conc. nitric acid, they are converted to the corresponding heterocyclic cations with loss of the exocyclic sulfur and selenium. This has been found to be also the case for 1,3-diaryltetrazolium-5-thiolates (**4**), and 1,3-diaryltetrazolium salts are isolated in good yields as stable tetrafluoroborates **5**. The corresponding tetraphenylborate **6a** is obtained by anion exchange of **5a** with sodium tetraphenylborate. Mercuration of tetrazolium salt **5** with mercury(II) acetate proceeds smoothly in dimethyl sulfoxide (DMSO) at 100°C to give bis(tetrazolio)mercury(II) **7**, whose protolysis with conc. hydrochloric acid gives back **5**. Replacement of the mercury atom of **7** by halogen is easily achieved by the



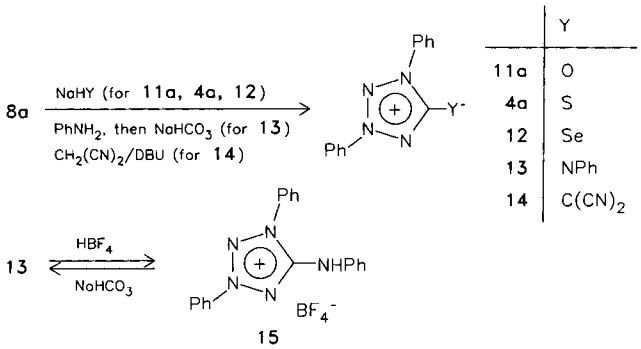
4 5 6 7

	R^1	R^2
a	Ph	Ph
b	*p*-MeC_6H_4	Ph
c	Ph	*p*-$MeOC_6H_4$

	X
8	Cl
9	Br
10	I

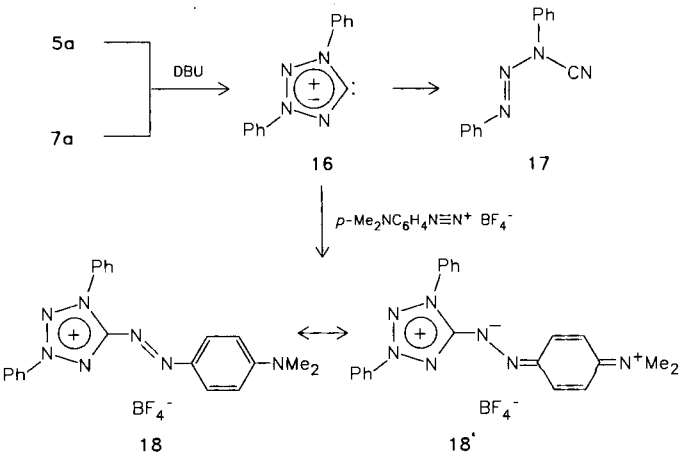
action of Cl_2, Br_2, and I_2 to afford 5-halotetrazolium salts **8–10**.

Compounds **8–10** are synthetically useful precursors of various mesoionic tetrazolium systems; for example, the chlorine atom of 5-chlorotetrazolium **8a** is smoothly replaced by nucleophiles such as OH, HS, and HSe anions to give quantitative yields of the corresponding olate **11a**, thiolate **4a**, and selenolate **12**, respectively. Furthermore, the reaction of **8** with aniline furnishes red crystals of tetrazolium-5-anilide **13** after treatment with base ($NaHCO_3$). Protonation of anilide **13** gives colourless 5-anilinotetrazolium salt **15**, which is reversively converted into anilide **13** upon base treatment. The selenolate **12** and anilide **13** have been obtained in this work for the first time[5]. The reaction of **8** with the conjugate base of malononitrile yields dicyanomethylide **14**. The reactions of other 5-halotetrazolium ions **9** and **10** with carbon nucleophiles will be discussed below.



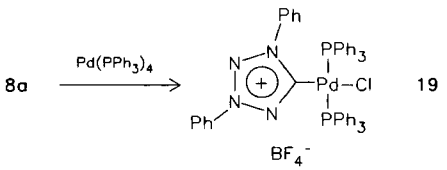
Deprotonation of 1,3-Diaryltetrazolium Ion and Chemical Trapping of 1,3-Diaryltetrazolylene

1,3-Diaryltetrazolylene (**16**) is an example of a mesoion-derived carbene **3**. The 1,3-diaryltetrazolium ion of **5** and **6** is the conjugate acid of **16**. The tetrazolium ring proton of **5** and **6** resonate at low magnetic field ($\delta = 11.2-11.3$). The coupling constant J_{C-H} between the tetrazolium ring carbon and proton is 235 Hz[6], indicating a considerable sp character of this carbon. Therefore, proton abstraction from **5** or **6** seems to be a suitable method for the generation of carbene **16**. Treatment of 1,3-diphenyltetrazolium ion **5a** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at room temperature gives 3-cyano-1,3-diphenyltriazene (**17**) in 73% yield. This compound has alternatively been prepared by coupling of phenylcyanamide with benzenediazonium chloride. The base-induced ring cleavage of 1,3-disubstituted tetrazolium ions to 3-cyanotriazenes has hitherto been reported for 1,3-dimethyl and 1-methyl-3-phenyltetrazolium ions[7]. Bis(1,3-diphenyltetrazolio)mercury (**7a**) also provides **17** in 79% yield upon reaction with DBU; **17** is considered to be a ring-opened product of the mesoionic carbene **16**. Unfortunately, all attempts have failed to characterize the intermediate **16**, generated by proton abstraction of **5** or **6**, by changing the base (e.g. butyllithium) and the solvent even at low temperature. However, derivatization of **16** by trapping with a diazonium salt has been realized[8]; *p*-(dimethylamino)benzenediazonium tetrafluoroborate readily reacts with **16** to yield the azo compound **18** in 69% yield. ^{13}C-NMR data suggest the significant contribution of the quinonoid structure **18'** to its ground state; two *ortho* carbons of the *p*-(dimethylamino)phenyl group as well as two *meta* carbons appear non-equivalently as broad signals owing to restricted rotation around the C-*ipso*–N-azo bond. Without DBU, tetrazolium salt **5a** does not react with the diazonium salt.



Preparation of a Palladium(II) Complex of 1,3-Diphenyltetrazolinydene

The mercury(II) complex **7** can be regarded as the first metal complex of a 1,3-diaryltetrazolinydene (**16**). In order to synthesize another example of the transition metal complex of **16**, oxidative addition of a low-valent transition metal complex to 5-halotetrazolium salt has been examined. When 5-chlorotetrazolium salt **8a** is treated with tetrakis-(triphenylphosphane)palladium(0), stable pale yellow crystals are obtained. Spectroscopic and analytical data indicate that this product is the cationic (1,3-diphenyltetrazolylene)-palladium(II) complex **19**. In the ^{13}C-NMR spectrum, the tetrazolium ring carbon appears at $\delta = 172.6$ as a triplet with J_{C-Pd-P} of 9.0 Hz, indicating that the two phosphane groups of **19** are *trans*-configurated[9]. Unfortunately, a similar reaction with tetrakis(triphenylphosphane)-platinum(0) does not give the expected platinum(II) complex. Several transition metal complexes of heterocyclic carbene are known[10]; however, mercury **7** and palladium complexes **19** are the first members of the complexes possessing a mesoion-derived carbene ligand **16**. These cationic compounds may be regarded as unique variations of mesoions, where the exocyclic group (f) in the general formula **1** of the mesoion is a metal atom.

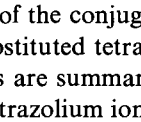
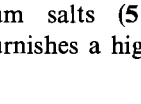


Reaction of 5-Substituted Tetrazolium Ions with Nucleophiles

As described above, 1,3-diphenyltetrazolium salt **5a** is converted into the ring-opened product **17** by the reaction

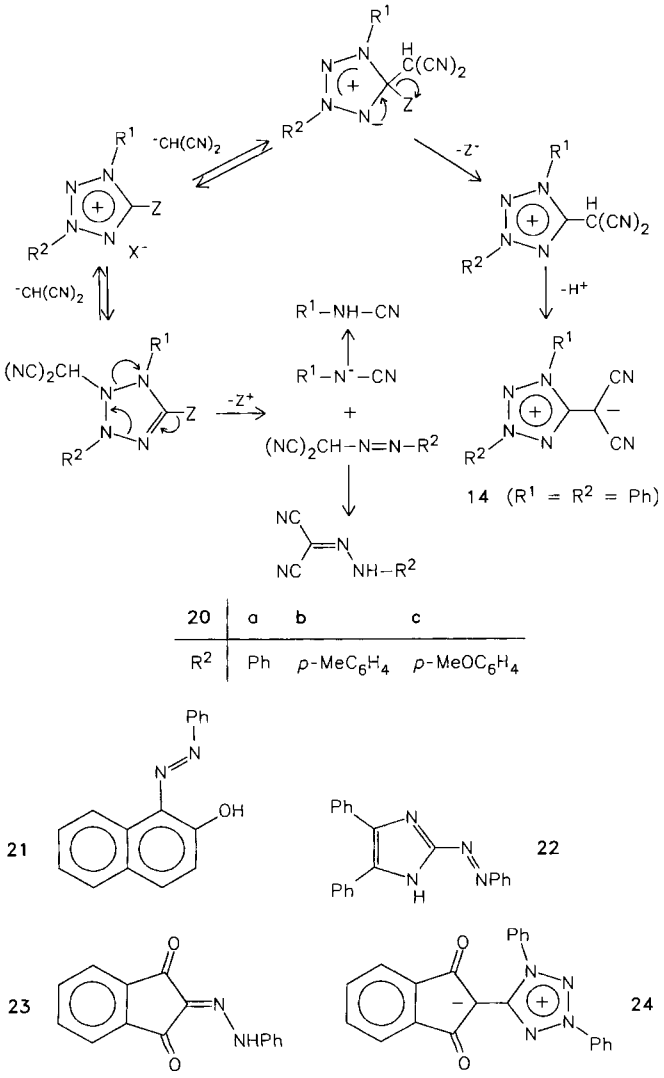
with DBU. On the other hand, when **5a** is treated with DBU in the presence of malononitrile, the phenylhydrazone (**20a**) of mesoxalonitrile is obtained in 71% yield together with phenylcyanamide (78%). Triazene **17** itself does not react with malononitrile in the presence of DBU. It is worth noting here again that chlorotetrazolium **8a** reacts with malononitrile to give dicyanomethylide **14**. Thus, the reaction of 5-substituted 1,3-diphenyltetrazolium salts with malononitrile gives two different products **14** and **20a**, depending on the substituent (Cl or H) on the tetrazolium ring. In order to examine the effect of the substituent at C-5 on the reaction course, nucleophilic reactions of the conjugate anion of malononitrile with various 5-substituted tetrazolium ions have been carried out. The results are summarized in Table 1. 5-Mercurio- (**7a**) and 5-iodotetrazolium ions (**10a**) as well as tetrazolium salt **5a** itself afford good yields of **20a** as major product together with phenylcyanamide. Next, for the purpose of determining whether the phenyl group of **20a** originates from the 1-phenyl or 3-phenyl group in the tetrazolium ions, the reactions with 3-phenyl-1-(*p*-tolyl)- (**5b**) and 3-(*p*-methoxyphenyl)-1-phenyltetrazolium salts (**5c**) has been examined. The former reaction furnishes a high yield of **20a**, and *p*-tolylhydrazone **20b** is not formed; whereas the product from the latter reaction is *p*-methoxyphenylhydrazone **20c** (71% yield). These results indicate that the nucleophilic attack occurs at N-2 and the aryl group attached to N-3 is transferred to the hydrazone **20**.

Table 1. Reaction of 5-substituted 1,3-diphenyltetrazolium salts with malononitrile

Tetrazolium	Substituent at C-5	Yield (%) 14	20a	PhNHCN
7a		0	72	34
5a	H	0	71	78
10a	I	0	54	63
9a	Br	71	16	16
8a	Cl	94	<1	0
25	OEt	95	0	0
26[a]		75	0	0

[a] Ditriflate was used; see ref.[3d].

Scheme 1



The total reaction pathway leading to **20** is illustrated in Scheme 1. Attack of the nucleophile at N-2 followed by fragmentation of the resulting intermediate, dihydrotetrazol, yields (arylazo)malononitrile and arylcyanamide anion. Prototropic rearrangement of (arylazo)malononitrile furnishes the more stable tautomer **20**. Compound **20** is known to be the coupling product of malononitrile and benzenediazonium[11], implying that **5**, **7**, and **10** can be synthetically used as benzenediazonium ion equivalents. Indeed, tetrazolium ion **5a** reacts with 2-naphthol and 4,5-diphenylimidazol to give good yields of 1-(phenylazo)-2-naphthol (**21**) and 4,5-diphenyl-2-(phenylazo)imidazol (**22**), respectively, hitherto prepared by coupling with benzenediazonium ion.

In contrast, 5-bromo- (**9a**), 5-chloro- (**8a**), and 5-ethoxytetrazolium ions (**25**) as well as the dicationic ether salt **26**[3d] are all converted into mesoionic dicyanomethylide **14** in high yields by nucleophilic substitution at the tetrazolium carbon C-5. Thus, it is evident that in the reactions of 5-substituted tetrazolium ions with nucleophiles the reaction pathway depends highly on the substituents of the tetrazolium C-5 atom. When the substituents are electropositive (e.g. Hg-tetrazolium, H, and I), the nucleophile tends to attack N-2 to yield phenylhydrazone **20** and phenylcyanamide, whereas when the substituents are eliminated as anions (e.g. Br^-, Cl^-, EtO^-, and tetrazolium–O^-), substitution occurs at C-5 to afford mesoionic methylide **14**[12]. The exact pathway, of course, depends on the type of the nucleophile used. The carbanion of 1,3-indanedione, for example, reacts with **5a**, **7a**, **10a**, and, in this case, even with bromotetrazolium **9a** to give phenylhydrazone **23** in high yields. The reactions of 5-chloro- (**8a**) and 5-ethoxytetrazolium ions (**25**)

as well as the dicationic ether **26** with 1,3-indanedione do not yield the corresponding methylide **24**, but only the hydrolysis product, i.e. tetrazolium-5-olate **11a**.

Experimental

Melting points: Hotstage apparatus, uncorrected. — MS (70 eV): Hitachi M-2000S. — IR (KBr): JASCO A-102. — ^{1}H NMR: Hitachi R-90 (90 MHz) or Varian XL-200 (200 MHz). — ^{13}C NMR: Varian XL-200 (50 MHz). ^{13}C-NMR data of the 1,3-diaryltetrazolium derivatives prepared in this paper are summarized in Table 2. — Elemental analyses: Elemental analysis Centre of Kyoto University.

3-(4-Methoxyphenyl)-1-phenyltetrazolium-5-olate (**11c**): According to ref.[13]. 1-(4-methoxyphenyl)-4-phenylthiosemicarbazide[14] (5.7 g, 21 mmol) was converted to **11c**; 4.8 g (82%) as colourless crystals, m.p. 182.5–183.5 °C (EtOH). — IR: $\tilde{\nu}$ = 1690 cm^{-1}, 1586, 1508, 1486, 1336, 1262, 1016, 836, 762. — ^{1}H NMR (90 MHz, $CDCl_3$): δ = 3.9 (s, 3H, OMe), 7.1 (d, J = 9 Hz, 2H, methoxyphenyl), 7.5 (m, 3H, Ph), 8.0 (m, 2H, Ph), 8.1 (d, J = 9 Hz, 2H, methoxyphenyl).

$C_{14}H_{12}N_4O_2$ (268.3)
Calcd. C 62.68 H 4.51 N 20.88
Found C 62.39 H 4.34 N 21.09

3-Phenyl-1-(p-tolyl)tetrazolium-5-thiolate (**4b**): 3-Phenyl-1-(*p*-tolyl)tetrazolium-5-olate (**11b**)[13] (4.9 g, 20 mmol) and Lawesson's reagent (5.7 g, 14 mmol) were allowed to react in refluxing toluene (250 ml) for 48 h according to ref.[3h], giving **4b**; 4.9 g (94%) as yellow crystals, m.p. 132–134 °C (MeOH). — IR: $\tilde{\nu}$ = 3040 cm^{-1}, 1590, 1510, 1485, 1365, 1320, 1300, 1260, 1180, 1170, 1010, 975, 915, 845, 810, 760, 700, 670. — ^{1}H NMR (90 MHz, $CDCl_3$): δ = 2.5 (s, 3H, Me), 7.5 (d, J = 9 Hz, 2H, tolyl), 7.7 (m, 3H, Ph), 8.0 (d, J = 9 Hz, 2H, tolyl), 8.2 (m, 2H, Ph).

$C_{14}H_{12}N_4S$ (268.3) Calcd. C 62.66 H 4.51
Found C 63.11 H 4.41

Table 2. ^{13}C-NMR data of 1,3-diaryltetrazolium derivatives prepared in this paper (δ values)

	Solvent	C-*i*	C-*o*	C-*m*	C-*p*	C$^+$	Other signals
4b	$CDCl_3$	131.2 135.1	120.1 124.0	129.6 129.8	131.9 140.8	174.4	21.2 (Me)
4c	[D$_6$]DMSO	128.4 134.0	122.5 125.3	115.3 129.2	130.4 161.8	173.4	55.9 (OMe)
5a	[D$_6$]DMSO	132.2 134.8	121.5 122.3	130.7 130.9	132.8 133.8	147.5	
5b	[D$_6$]DMSO	129.9 134.8	121.4 122.0	130.9 131.0	133.7 143.3	147.2	20.9 (Me)
5c	[D$_6$]DMSO	127.7 132.3	122.2 123.4	115.9 130.7	132.6 163.1	147.1	56.2 (OMe)
7a	[D$_6$]DMSO	134.2 135.1	121.6 124.7	130.5 130.9	132.6 133.4	183.3	
7b	[D$_6$]DMSO	131.8 135.1	121.6 124.4	130.7 130.9	133.3 142.7	183.3	20.9 (Me)
7c	[D$_6$]DMSO	128.0 134.2	123.4 124.7	115.9 130.4	132.4 162.8	183.0	56.2 (OMe)
8a	[D$_7$]DMF	132.5 136.7	123.2 127.5	132.4 132.6	135.4 135.9	153.9	
9a	[D$_7$]DMF	—[a] —[a]	123.2 127.9	132.4 132.7	135.3 135.9	143.2	
10a	[D$_6$]DMSO	133.9 134.5	121.4 126.4	130.5 131.0	132.4 133.3	117.3	
10b	[D$_6$]DMSO	130.0 134.5	121.4 126.1	130.8 131.0	133.9 143.7	117.2	21.1 (Me)
10c	[D$_6$]DMSO	127.5 132.5	123.3 126.4	115.9 130.4	133.2 163.1	116.8	56.2 (OMe)
11c	$CDCl_3$	129.5 134.2	120.1 121.3	114.6 129.3	128.2 161.7	159.2	55.6 (OMe)
12	$CDCl_3$	134.1 134.8	120.2 124.7	129.1 129.9	130.7 132.2	167.4	
13	$CDCl_3$	135.1 136.1	121.2 122.7	128.4 129.0	127.8 131.1	154.3	119.9 (C-*o* of PhN$^-$) 120.6 (C-*p* of PhN$^-$) 129.5 (C-*m* of PhN$^-$) 148.8 (C-*i* of PhN$^-$)
18	[D$_6$]DMSO	132.5 135.4	121.3 125.4	130.2 130.9	132.1 133.5	162.0	41.2 (NMe) 113.9[b] (C-*m*, $C_6H_4NMe_2$) 115.9[b] (C-*m*, $C_6H_4NMe_2$) 120.4[b] (C-*o*, $C_6H_4NMe_2$) 141.0[b] (C-*o*, $C_6H_4NMe_2$) 145.5 (*C*–NMe_2) 158.2 (C–N=N–)
19	$CDCl_3$	134.3 134.9	120.6 122.3	130.3 130.5	132.4 133.3	172.6[c]	127.9[d] (C-*i* of Ph_3P) 128.9 (C-*o* of Ph_3P) 131.7 (C-*p* of Ph_3P) 133.8 (C-*m* of Ph_3P)

[a] Not observed owing to rapid hydrolysis. — [b] Broad signal. — [c] t, J_{C-Pd-P} = 9.0 Hz. — [d] J_{C-P} = 25.6 Hz.

3-(4-Methoxyphenyl)-1-phenyltetrazolium-5-thiolate (**4c**): Analogously to the preceding reaction, **11c** (1.1 g, 4.1 mmol) and Lawesson's reagent (1.4 g, 3.3 mmol) were allowed to react, giving **4c**; 1.1 g (90%) as yellow crystals, m.p. 164–166°C (MeOH). – IR: $\tilde{\nu}$ = 1586 cm^{-1}, 1508, 1490, 1366, 1300, 1262, 1180, 1016, 838, 764, 688. – ^1H NMR (90 MHz, [D_6]DMSO): δ = 3.9 (s, 3H, OMe), 7.2 (d, *J* = 9 Hz, 2H, methoxyphenyl), 7.6 (m, 3H, Ph), 8.0 (m, 2H, Ph), 8.1 (d, *J* = 9 Hz, 2H, methoxyphenyl).

$C_{14}H_{12}N_4OS$ (284.3)
Calcd. C 59.14 H 4.25 N 19.70
Found C 59.19 H 4.38 N 19.63

1,3-Diphenyltetrazolium Tetrafluoroborate (**5a**): 1,3-Diphenyltetrazolium-5-thiolate (**4a**)[12b] (19 g, 75 mmol) was added portionwise to well stirred conc. nitric acid (60 ml) with cooling in a water bath. The mixture was then heated at 100°C for 1 h, and, while hot, poured into aqueous sodium tetrafluoroborate (22 g, 200 ml). A pale yellow precipitate deposited immediately, and the mixture was kept overnigth in a refrigerator. The precipitate was filtered, washed with water, and recrystallized from methanol (300 ml) to yield **5a**; 20.7 g (89%) as colourless crystals, m.p. 177–178°C (MeOH). – IR: $\tilde{\nu}$ = 3140 cm^{-1}, 2920, 1505, 1490, 1461, 1272, 1130–1030, 768, 714, 682. – ^1H NMR (200 MHz, [D_6]acetone): δ = 7.9 (m, 6H, Ph), 8.2–8.4 (m, 4H, Ph), 11.3 (s, 1H, C^+–H).

$C_{13}H_{11}BF_4N_4$ (310.1)
Calcd. C 50.35 H 3.58 N 18.01
Found C 50.15 H 3.68 N 18.14

3-Phenyl-1-(p-tolyl)tetrazolium Tetrafluoroborate (**5b**): Analogously to the preceding reaction, **4b** (2.0 g, 7.5 mmol) was converted to **5b**; 1.5 g (61%) as pale yellow crystals, m.p. 186–188°C (EtOH). – IR: $\tilde{\nu}$ = 3450 cm^{-1}, 2820, 1270, 1120, 1080, 1035, 820, 760, 670. – ^1H NMR (90 MHz, [D_6]DMSO): δ = 2.5 (s, 3H, Me), 7.7 (d, *J* = 9 Hz, 2H, tolyl), 7.9 (m, 3H, Ph), 8.1 (d, *J* = 9 Hz, 2H, tolyl), 8.3 (m, 2H, Ph), 11.2 (s, 1H, C^+–H).

$C_{14}H_{13}BF_4N_4$ (324.1) Calcd. C 51.88 H 4.04
Found C 51.59 H 3.99

3-(4-Methoxyphenyl)-1-phenyltetrazolium Tetrafluoroborate (**5c**): Analogously to the reaction with **4a**, **4c** (720 mg, 2.5 mmol) was converted to **5c**; 558 mg (66%) as colourless crystals, m.p. 172–175°C (EtOH). – IR: $\tilde{\nu}$ = 3140 cm^{-1}, 1588, 1500, 1262, 1172, 1118, 1080, 1124, 834, 764, 680. – ^1H NMR (90 MHz, [D_6]DMSO): δ = 3.9 (s, 3H, OMe), 7.4 (d, *J* = 9 Hz, 2H, methoxyphenyl), 7.8 (m, 3H, Ph), 8.2 (m, 2H, Ph), 8.3 (d, *J* = 9 Hz, 2H, methoxyphenyl), 11.2 (s, 1H, C^+–H).

$C_{14}H_{13}BF_4N_4O$ (340.1)
Calcd. C 49.44 H 3.85 N 16.47
Found C 49.02 H 3.67 N 16.48

1,3-Diphenyltetrazolium Tetraphenylborate (**6a**) was obtained by anion exchange of **5a**: A solution of **5a** (310 mg, 1 mmol) in acetonitrile (2 ml) was mixed with sodium tetraphenylborate (342 mg, 1 mmol) in water (2 ml). A yellow precipitate was immediately formed, which was filtered and dried. Recrystallization from MeCN/Et_2O gave pure **6a**; 533 mg (98%) as yellow crystals, m.p. 156°C (dec). – IR: $\tilde{\nu}$ = 3120 cm^{-1}, 3050, 1576, 1480, 1424, 1266, 758, 732, 706, 680. – ^1H NMR (60 MHz, [D_6]DMSO): δ = 6.9 (m, 12H, Ph), 7.2 (m, 8H, Ph), 7.8 (m, 6H, Ph), 8.1 (m, 2H, Ph), 8.3 (m, 2H, Ph), 11.2 (s, 1H, C^+–H).

$C_{37}H_{31}BN_4$ (542.5)
Calcd. C 81.92 H 5.76 N 10.33
Found C 81.92 H 5.62 N 10.31

Bis(1,3-diphenyltetrazolio)mercury(II) Bis(Tetrafluoroborate) (**7a**): A mixture of **5a** (46.2 g, 149 mmol) and mercury(II) acetate (26.1 g, 82 mmol) was heated at 100°C for 1 h in DMSO (150 ml). After cooling to room temp., the mixture was poured into aqueous sodium tetrafluoroborate (150 g in 3 l of water). After storage overnight in a refrigerator, the precipitate was filtered and washed with a small amount of ethanol to give **7a**; 50 g (82%) as pale beige powder, m.p. ca. 290°C (dec.). – IR: $\tilde{\nu}$ = 3070 cm^{-1}, 1588, 1488, 1130–1020, 924, 768, 680. – ^1H NMR (90 MHz, [D_6]DMSO): δ = 7.8 (m, 16H, Ph), 8.3 (m, 4H, Ph).

$C_{26}H_{20}B_2F_8HgN_8$ (818.8)
Calcd. C 38.14 H 2.46 N 13.69
Found C 37.65 H 2.41 N 13.48

Bis[3-phenyl-1-(p-tolyl)tetrazolio]mercury(II) Bis(tetrafluoroborate) (**7b**): Analogously to the preceding reaction, **5b** (2.3 g, 7.1 mmol) was converted to **7b**; 2.2 g (76%) as pale beige powder, m.p. 211–212°C (dec.). – IR: $\tilde{\nu}$ = 3080 cm^{-1}, 1600, 1510, 1490, 1360, 1290, 1240, 1130, 1050, 820, 765, 700, 680. – ^1H NMR (90 MHz, [D_6]DMSO): δ = 2.5 (s, 3H, Me), 7.5 (d, *J* = 9 Hz, 2H, tolyl), 7.9 (m, 5H, tolyl and Ph), 8.3 (m, 2H, Ph).

$C_{28}H_{24}B_2F_8HgN_8$ (846.8)
Calcd. C 39.72 H 2.86 N 13.23
Found C 37.78 H 2.88 N 12.41

Bis[3-(4-methoxyphenyl)-1-phenyltetrazolio]mercury(II) Bis(tetrafluoroborate) (**7c**): Analogously to the reaction with **5a**, **5c** (880 g, 2.6 mmol) was converted to **7c**; 648 mg (56%) as pale beige powder, m.p. ca. 175°C (dec.) (EtOH). – IR: $\tilde{\nu}$ = 1594 cm^{-1}, 1512, 1494, 1270, 1172, 1060, 1024, 816, 770, 704, 696. – ^1H NMR (90 MHz, [D_6]DMSO): δ = 3.9 (s, 6H, OMe), 7.4 (d, *J* = 9 Hz, 4H, methoxyphenyl), 7.7 (m, 6H, Ph), 8.0 (m, 4H, Ph), 8.3 (d, *J* = 9 Hz, 4H, methoxyphenyl).

$C_{28}H_{24}B_2F_8HgN_8O_2$ (878.8)
Calcd. C 38.27 H 2.75 N 12.75
Found C 37.74 H 2.63 N 12.70

5-Chloro-1,3-diphenyltetrazolium Tetrafluoroborate (**8a**): Chlorine, generated from potassium permanganate (4.7 g, 30 mmol) and hydrochloric acid (36 ml), was bubbled during ca. 3 h through a suspension of **7a** (740 mg, 0.9 mmol) in dichloromethane (10 ml). Ether (80 ml) was added, and the mixture was stirred at room temp. for 30 min. The formed precipitate was filtered off and washed with ethanol (50 ml). Recrystallization from MeCN/AcOEt gave **8a**; 362 mg (59%) as colourless crystals, m.p. 185–188°C (dec.) (MeCN/AcOEt). This compound was rapidly hydrolyzed to the corresponding olate **11a** when dissolved in moist DMSO. – IR: $\tilde{\nu}$ = 1490 cm^{-1}, 1452, 1334, 1274, 1208, 1060, 768, 684. – ^1H NMR (90 MHz, [D_7]DMF): δ = 8.0 (m, 8H, Ph), 8.4 (m, 2H, Ph).

$C_{13}H_{10}BClF_4N_4$ (344.6)
Calcd. C 45.32 H 2.93 N 16.26
Found C 45.16 H 2.97 N 16.24

5-Bromo-1,3-diphenyltetrazolium Tetrafluoroborate (**9a**): To a suspension of **7a** (753 mg, 0.9 mmol) in dichloromethane (10 ml) bromine (0.2 ml, 4 mmol) was added. The mixture was stirred at room temp. for 18 h. Ether (80 ml) was added, and the formed precipitate was filtered and washed with ether. Recrystallization from MeCN/AcOEt gave **9a**; 377 mg (54%) as colourless crystals, m.p. 207–209°C (dec.) (MeCN/AcOEt). This compound rapidly hydrolyzes to **11a** when dissolved in moist DMSO. – IR: $\tilde{\nu}$ = 1488 cm^{-1}, 1438, 1264, 1082, 1036, 764, 686. – ^1H NMR (90 MHz, [D_7]DMF): δ = 8.0 (m, 8H, Ph), 8.4 (m, 2H, Ph).

$C_{13}H_{10}BBrF_4N_4$ (389.0)
Calcd. C 40.14 H 2.59 N 14.40
Found C 40.18 H 2.55 N 14.51

5-Iodo-1,3-diphenyltetrazolium Tetrafluoroborate (**10a**): To a suspension of **7a** (2.51 g, 3.1 mmol) in dichloromethane (30 ml) iodine (1.65 g, 6.5 mmo) was added. The mixture was stirred at room temp. for 1 h. Ether (50 ml) was added, and the mixture was kept in a refrigerator. The formed precipitate was filtered and washed with ether. Recrystallization from methanol (80 ml) gave crystals (1.8 g) of **10a**. From the mother liquor, a second crop of the product was obtained (0.3 g): total yield 2.1 g (78%) as colourless crystals, m.p. 212–215°C (MeOH). – IR: $\tilde{\nu}$ = 3090 cm^{-1}, 1498, 1492, 1426, 1256, 1130–1020, 998, 766, 686, 678. – ^1H NMR (200 MHz, [D_6]-DMSO): δ = 7.90 (m, 8H, Ph), 8.32 (m, 2H, Ph).

$C_{13}H_{10}BF_4IN_4$ (436.0)
Calcd. C 35.81 H 2.31 N 12.85
Found C 36.08 H 2.13 N 12.94

5-Iodo-3-phenyl-1-(p-tolyl)tetrazolium Tetrafluoroborate (**10b**): Analogously to the preceding reaction, **7b** (750 mg, 0.89 mmol) was converted to **10b**; 560 mg (71%) as colourless crystals, m.p. 216–218°C (MeOH). – IR: $\tilde{\nu}$ = 3130 cm^{-1}, 2920, 1600, 1510, 1490, 1460, 1395, 1325, 1290, 1270, 1060, 820, 780, 700, 670. – ^1H NMR (90 MHz, [D_6]DMSO): δ = 2.5 (s, 3H, Me), 7.7 (d, *J* = 9 Hz, 2H, tolyl), 7.8 (d, *J* = 9 Hz, 2H, tolyl), 7.9 (m, 3H, Ph), 8.3 (m, 2H, Ph).

$C_{14}H_{12}BF_4IN_4$ (450.0)
Calcd. C 37.37 H 2.69 N 12.45
Found C 36.95 H 2.59 N 12.38

5-Iodo-3-(4-methoxyphenyl)-1-phenyltetrazolium Tetrafluoroborate (**10c**): Analogously to the reaction with **7a**, **7c** (440 mg, 0.50 mmol) was converted to **10c**; 290 mg (62%) as colourless crystals, m.p. 188–190°C (MeCN/Et_2O). – IR: $\tilde{\nu}$ = 1592 cm^{-1}, 1510, 1264, 1174, 1084, 838, 766, 684. – ^1H NMR (90 MHz, [D_6]DMSO): δ = 3.9 (s, 3H, Me), 7.3 (d, *J* = 9 Hz, 2H, methoxyphenyl), 7.9 (m, 5H, Ph), 8.2 (d, *J* = 9 Hz, 2H, methoxyphenyl).

$C_{14}H_{12}BF_4IN_4O$ (466.0)
Calcd. C 36.09 H 2.60 N 12.02
Found C 36.27 H 2.56 N 12.13

Reaction of Chlorotetrazolium Salt **8a** *with OH, HS, and HSe Anions:* To a solution of **8a** (35 mg, 0.1 mmol) in DMF (2 ml) was added sodium hydroxide (8 mg, 0.2 mmol) in water (1 ml), and the mixture was stirred for 5 min. Water was then added, and the product was extracted several times with dichloromethane. The combined extracts were washed with water and dried (Na_2SO_4). The solvent was removed under reduced pressure to leave olate **11a** (22 mg, 92%). Similarly, the reaction of **8a** (35 mg, 0.1 mmol) with sodium hydrogen sulfide (170 mg, 3 mmol) in DMF (3 ml) for 5 min gave thiolate **4a** (25 mg, 100%).

1,3-Diphenyltetrazolium-5-selenolate (**12**): To a solution of sodium hydrogen selenide, prepared from selenium (66 mg, 0.84 mmol) and $NaBH_4$ (32 mg, 0.84 mmol) in ethanol (2 ml) according to ref.[15], chlorotetrazolium **8a** (75 mg, 0.22 mmol) was added. The mixture was ultrasonicated for 5 min. The solvent was removed under reduced pressure and the residue chromatographed on silica gel (eluent: dichloromethane) to give selenolate **12**; 65 mg (100%) as orange crystals, m.p. 158°C (dec.) (benzene). When iodotetrazolium **10a** was used in place of **8a**, the yield dropped to 77%. – MS: *m/z* 301 [M^+]. – IR: $\tilde{\nu}$ = 1490 cm^{-1}, 1366, 1312, 1264, 1174, 1154, 766, 754, 688. – ^1H NMR (90 MHz, $CDCl_3$): δ = 7.6 (m, 6H, Ph), 8.1 (m, 4H, Ph).

$C_{13}H_{10}N_4Se$ (301.2)
Calcd. C 51.84 H 3.35 N 18.60
Found C 51.86 H 3.18 N 18.77

Reaction of Chlorotetrazolium Salt **8a** *with Aniline:* Salt **8a** (70 mg, 0.2 mmol) was suspended in chloroform (2 ml), and aniline (0.3 ml, 4 mmol) was added. The mixture was warmed until all the tetrazolium salt had dissolved, and then it was kept at room temp. for 3 h. The solvent was removed, and the residue was washed with ether. The residue was then dissolved in dichloromethane (30 ml) and the solution shaken with a sat. aqueous sodium hydrogen carbonate solution, a deep red colour developed immediately. The dichloromethane layer was separated and dried (Na_2SO_4). The solvent was evaporated, and the residue was recrystallized from CH_2Cl_2/hexane to give *1,3-diphenyltetrazolium-5-anilide* (**13**): 53 mg (85%) as dark red crystals, m.p. 132°C. – MS: *m/z* 313 [M^+]. – IR: $\tilde{\nu}$ = 1630 cm^{-1}, 1580, 1484, 1332, 760, 694. – ^1H NMR (90 MHz, $CDCl_3$): δ = 6.9 (m, 1H, Ph), 7.5 (m, 10H, Ph), 8.2 (m, 2H, Ph), 8.4 (m, 2H, Ph).

$C_{19}H_{15}N_5$ (313.4)
Calcd. C 72.83 H 4.82 N 22.35
Found C 73.12 H 4.69 N 22.41

1,3-Diphenyltetrazolium-5-dicyanomethylide (**14**): To a mixture of **8a** (123 mg, 0.36 mmol) and malononitrile (30 mg, 0.45 mmol) in dichloromethane (5 ml) DBU (0.12 ml, 0.8 mmol) was added. After stirring for 2 h, the mixture was subjected to column chromatography on silica gel. Elution with chloroform gave **15** (97 mg, 94%), identified by direct comparison with an authentic sample[3d]. A trace amount (<1%) of **20a** were detected by TLC.

5-Anilino-1,3-diphenyltetrazolium Tetrafluoroborate (**15**): Five drops of tetrafluoroboric acid (42%) were added to a solution of anilide **13** (70 mg, 0.22 mmol) in methanol (15 ml). The red colour of the reaction mixture changed to yellow orange. The solution was concentrated in vacuo, and ether was added to the residue. White crystals formed which were separated by filtration and recrystallized from ethanol to afford **15** as monohydrate: 76 mg (83%) as colourless crystals, m.p. 196°C. – IR: $\tilde{\nu}$ = 3660 cm^{-1}, 3530, 3060, 1640, 1588, 1494, 1112, 1074, 1038, 756, 686. – ^1H NMR (90 MHz, CD_3CN): δ = 2.2 (bs, 1H, NH), 7.1–8.0 (m, 13H, Ph), 8.2 (m, 2H, Ph).

$C_{19}H_{16}BF_4N_5 \cdot H_2O$ (419.2)
Calcd. C 54.44 H 4.33 N 16.71
Found C 54.67 H 4.47 N 16.79

Deprotonation of 1,3-Diphenyltetrazolium Salt **5a**: *3-Cyano-1,3-diphenyltriazene* (**17**): To a suspension of **5a** (540 mg, 1.63 mmol) in dichloromethane (60 ml) was added DBU (0.75 ml, 5 mmol), and the mixture was stirred at room temp. for 2 h. Column chromatography (silica gel, dichloromethane) gave crude **17**. A pure sample of **17** was obtained as the hemihydrate after recrystallization from benzene; 234 mg (62%) as orange crystals, m.p. 146–147°C. – IR: $\tilde{\nu}$ = 3400 cm^{-1}, 3160, 2900, 2225, 1604, 1514, 1304, 1258, 1158, 1072, 832, 760, 716, 680. – ^1H MNR (90 MHz, $CDCl_3$): δ = 7.16 (m, 2H, Ph), 7.48 (m, 4H, Ph), 7.92 (m, 4H, Ph). – ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 111.6 (CN), 115.7, 122.4, 124.8, 129.5, 131.2 (C-*p*), 142.0 (C-*p*), 147.5 (C-*i*), 152.0 (C-*i*).

$C_{13}H_{10}N_4 \cdot (1/2)H_2O$ (231.3)
Calcd. C 67.51 H 4.80 N 24.23
Found C 67.84 H 4.78 N 24.07

Alternatively **17** was prepared by coupling of benzenediazonium chloride with phenylcyanamide: A solution of benzenediazonium chloride, prepared from aniline (0.70 g, 15 mmol), sodium nitrite (0.55 g, 8.0 mmol), and hydrochloric acid (2 ml) in water (9 ml), was added to a mixture of phenylcyanamide[16] (0.89 g, 7.5 mmol) and sodium hydroxide (3.55 g) in water (90 ml) at 0–5°C. Additional sodium hydroxide (11.8 g) in water (10 ml) was added, and the mixture was stirred for 3 h. The product was extracted with dichloromethane, and the extract was dried (Na_2SO_4). The solvent was evaporated, and the residue was chromatographed on silica gel

(dichloromethane). Recrystallization from benzene gave pure **17** (0.68 g, 39%).

5-[4-(Dimethylamino)phenylazo]-1,3-diphenyltetrazolium Tetrafluoroborate (**18**): To a mixture of **5a** (103 mg, 0.33 mmol) and 4-(dimethylamino)phenylbenzenediazonium tetrafluoroborate[17] (280 mg, 1.2 mmol) in acetonitrile (3 ml) DBU (0.1 ml, 0.67 mmol) was added at −30°C, and the reaction mixture was allowed to warm to room temp. After stirring for 1 h at room temp., the solvent was evaporated under reduced pressure. The residual solid was washed with ether and recrystallized from MeCN/EtOH giving **18**; 109 mg (69%) as purple crystals, m.p. 186°C (dec.). – IR: $\tilde{\nu} = 1616\ cm^{-1}$, 1514, 1306, 1256, 1154, 1054, 990, 820, 766. – ^1H NMR (200 MHz, CD_3CN): $\delta = 3.4$ (s, 6H, Me), 7.0 (br. d, $J = 9$ Hz, 2H, H-*m* of aminophenyl), 7.8 (m, 6H, Ph), 7.9 (br. m, 2H, H-*o* of aminophenyl), 8.0 (m, 2H, Ph), 8.3 (m, 2H, Ph).

$C_{21}H_{20}BF_4N_7 \cdot 1/2(C_2H_5OH)$ (480.3)
Calcd. C 55.02 H 4.83 N 20.42
Found C 55.03 H 4.61 N 19.95

trans-Chloro(1,3-diphenyltetrazolylene)bis(triphenylphosphane)-palladium(II) Tetrafluoroborate (**19**): A mixture of **8a** (35 mg, 0.10 mmol) and tetrakis(triphenylphosphane)palladium(0) (116 mg, 0.10 mmol) in chloroform (5 ml) was heated at reflux for 1.5 h. The solvent was evaporated, the residue was washed with ether and recrystallized from MeCN/Et_2O to yield **19**; 86 mg (88%) as pale yellow crystals, m.p. 184°C (dec.). – IR: $\tilde{\nu} = 3060\ cm^{-1}$ 1480, 1434, 1382, 1310, 1240, 1158, 1090, 746, 696. – ^1H NMR (90 MHz, $CDCl_3$): $\delta = 7.4$ (m, 30H, PPh_3), 7.7 (m, 8H, Ph), 8.1 (m, 2H, Ph).

$C_{49}H_{40}BClF_4N_4P_2Pd$ (975.5)
Calcd. C 60.33 H 4.13 N 5.74
Found C 59.79 H 4.09 N 6.08

Reaction of 5-Substituted 1,3-Diaryltetrazolium Salts with Malononitrile: The following reaction of 1,3-diphenyltetrazolium salt **5a** is representative. To a solution of **5a** (155 mg, 0.50 mmol) and malononitrile (33 mg, 0.50 mmol) in dichloromethane (5 ml) DBU (0.15 ml, 1.0 mmol) was added, and the mixture was stirred at room temp. for 2 h. It was subsequently subjected to column chromatography on silica gel. Elution with dichloromethane yielded **20a** and phenylcyanamide (46 mg, 78%).

(Phenylhydrazono)malononitrile (**20a**): 60 mg (71%), orange crystals, m.p. 136°C (dec.) (ref.[11] 139–145°C, dec.).

Results for other 5-substituted 1,3-diaryltetrazolium salts are summarized in Table 1. The reaction of 3-phenyl-1-(p-tolyl)tetrazolium salt **5b** also gave **20a**, whereas 3-(4-methoxyphenyl)-1-phenyltetrazolium salt **5c** afforded **20c** (71%) and phenylcyanamide (44%).

(4-Methoxyphenylhydrazono)malononitrile (**20c**): 71 mg (71%) as yellow crystals, m.p. 140–144°C (ref.[18] 149°C).

Reaction of 1,3-Diphenyltetrazolium Salt **5a** *with 2-Naphthol:* To a mixture of **5a** (62 mg, 0.2 mmol) and 2-naphthol (58 mg, 0.4 mmol) in dichloromethane (5 ml) DBU (0.1 ml, 0.6 mmol) was added, and the mixture was stirred at room temp. for 30 min. It was then subjected to column chromatography on silica gel (eluent: dichloromethane). A red band was collected and recrystallized from ethanol to give *1-(phenylazo)-2-naphthol* (**21**); 50 mg (100%) as red crystals, m.p. 130°C (ref.[19] 134°C).

Reaction of 1,3-Diphenyltetrazolium Salt **5a** *with 4,5-Diphenylimidazole:* To a mixture of **5a** (40 mg, 0.13 mmol) and 4,5-diphenylimidazole (29 mg, 0.13 mmol) in dichloromethane (3 ml) DBU (0.06 ml, 0.4 mmol) was added, and the mixture was stirred at room temp. for 1 h. It was subsequently subjected to column chromatography on silica gel (eluent: dichloromethane) to give *4,5-diphenyl-2-(phenylazo)imidazol* (**22**); 29 mg (69%) as orange crystals, m.p. 215–216°C (ref.[20] 222°C).

Reaction of 5-Substituted 1,3-Diaryltetrazolium Salts with 1,3-Indanedione: The following reaction of 5-iodo-1,3-diphenyltetrazolium **10a** is representative. To a mixture of **11a** (44 mg, 0.10 mmol) and 1,3-indanedione (15 mg, 0.10 mmol) in dichloromethane (5 ml) DBU (0.05 ml, 0.36 mmol) was added. After stirring for 1.5 h at room temp., the mixture was purified by column chromatography (SiO_2, CH_2Cl_2) to give *2-(phenylhydrazono)-1,3-indanedione* (**23**): 24 mg (96%) as yellow crystals, m.p. 192°C (ref.[21] 192–193°C).

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[402/92]