transferred to a separatory funnel containing brine (10 mL). The mixture was extracted with chloroform (6 × 10 mL), and then the combined extracts were dried over $MgSO_4$. The solvent was evaporated and the residue was purified by reverse-phase chromatography (Water Delta Prep, 30 cm × 30 mm C_{18} Delta Pak column, 80% water/methanol to 40% water/methanol over 10 min, 40% water/methanol to 100% methanol over 15 min) to provide syn oxime **28** (10 mg, 6% yield) and the desired anti oxime **29** (82 mg, 53% yield) as colorless oils: ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.42 (br s, 1 H), 7.30–7.18 (m, 6 H), 4.12 (m, 3 H), 3.65–2.74 (m, 6 H), 2.59–1.02 (m, 8 H), 1.69 (s, 3 H), 1.24 (t, J = 5.5 Hz, 3 H).

[(±)-2α,4α,6α]-6-[(Acetylamino)methyl]-9-oxo-2-phenyl-1*H*-perhydroazonine-4-acetic Acid Ethyl Ester (30). *p*-Toluenesulfonyl chloride (63 mg, 0.33 mmol) in anhydrous methylene chloride (1 mL) was added dropwise over 20 min to a solution of **29** (82 mg, 0.22 mmol) and pyridine (36 μL, 0.44 mmol) in 2 mL of methylene chloride at 0 °C. The mixture was stirred at 0 °C for 5 h and then poured into cold 5% HCl (5 mL). The slurry was extracted with chloroform (5 × 5 mL), and the extracts were dried over $MgSO_4$. The chloroform was evaporated, and the residue was taken up in tetrahydrofuran (3 mL). Potassium carbonate (50 mg, 0.36 mmol) in water (3 mL) was added, and the reaction was stirred overnight at room temperature. The reaction mixture was transferred to a separatory funnel and extracted with chloroform (5 × 5 mL). The extracts were dried over $MgSO_4$, and then the solvent was evaporated. The residue was purified by reverse-phase HPLC (Waters Delta Prep, 30 cm × 30 mm C_{18} Delta Pak column, 65% methanol/water) to afford **30** (25 mg, 30% yield) as a colorless oil: IR ($CHCl_3$) 3445, 3370, 1719, 1662, 1520, 700 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ 7.41–7.20 (m, 5 H), 5.22 (d, J = 9.5 Hz, 0.25 H), 5.03 (d, J = 9.5 Hz, 0.25 H), 4.18–4.08 (m, 2 H), 3.72–3.66 (m, 0.25 H), 3.57–3.52 (m, 0.25 H), 3.10–2.90 (m, 2 H), 1.96 (s, 0.18 of CH_3), 1.95 (s, 0.5 of CH_3), 1.93 (s, 0.32 of CH_3), 1.26–1.21 (m, 3 H); MS (70 eV) m/e (relative intensity) 374 (M^+, 23), 329 (9), 287 (11), 260 (18), 198 (6), 140 (19), 106 (100), 91 (32), 43 (37); HRMS (EI) calcd for $C_{21}H_{30}N_2O_4$ (M^+) 374.2206, found 375.2185. Temperature-dependent ^{1}H NMR spectra of **30** in $CDCl_3$ are described in the text and Figure 4.

Acknowledgment. We thank members of our Physical Chemistry Department for obtaining spectral and microanalytical data, especially Mr. Louis J. Todaro and Ms. Ann-Marie Chiu for performing the X-ray crystallography analyses, and Dr. Thomas J. Williams and Mr. Gino J. Sasso for assistance with NMR studies.

Registry No. (±)-**3**, 123836-24-8; (±)-**4**, 123836-25-9; (±)-**5**, 123836-26-0; (±)-**6**, 123930-04-1; (±)-**7**, 123836-27-1; (±)-**8**, 123930-05-2; (±)-**8** (*O*-tosyl derivative), 123836-50-0; (±)-**9**, 123836-28-2; (±)-**10**, 123836-29-3; (±)-**11**, 123836-30-6; (±)-**12**, 123836-31-7; (±)-**13**, 123836-32-8; (±)-**14**, 123836-33-9; (±)-**15**, 123836-34-0; (±)-**16**, 123930-06-3; (±)-1α,5α,6α-**17**, 123836-35-1; (±)-1α,5β,6β-**17**, 123836-46-4; (±)-1α,6α-**18**, 123836-36-2; (±)-1α,6β-**18**, 123836-47-5; (±)-1α,6α-**19**, 123836-37-3; (±)-1α,6β-**19**, 123836-48-6; (±)-1α,6α-**20**, 123836-38-4; (±)-1α,6β-**20**, 123836-49-7; **21**, 123836-39-5; **22**, 123836-40-8; **23**, 123836-41-9; (±)-**24**, 123836-42-0; (±)-**25**, 123930-07-4; (±)-**26**, 123930-08-5; (±)-**27**, 123930-09-6; (±)-**28**, 123836-43-1; (±)-**29**, 123836-44-2; (±)-**30**, 123836-45-3; PhLi, 591-51-5; MeI, 74-88-4; $MeNO_2$, 75-52-5; $HOCH_2CH_2OH$, 107-21-1; $(EtO)_2P(O)CH_2COOEt$, 867-13-0; (*Z*)-*cis*-1,5-cyclooctadiene monoepoxide, 19740-90-0; (*Z*,*Z*)-2,6-cyclooctadien-1-one, 31351-00-5.

Supplementary Material Available: Tables I–XII of crystal data, experimental details, bond lengths, bond angles, torsion angles, and equivalent isotropic thermal factors for lactam **9** at 295 and 110 K and Table XIII listing conformational energies and root-mean-square fits for **30** to each of the model β-turn types (9 pages). Ordering information is given on any current masthead page.

In Situ Generation of 2,3-Diaryltetrazolinylidenes: Trapping Experiments and Ring Opening to 1-Cyanoazimines†

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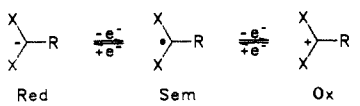
Abstract: The redox system formazanide ion/tetrazolium ion, realized as an ECE sequence, is conceived as a general device to manipulate both electron-deficient and -surplus centers attached to the carbon atom of this system electronically. In order to introduce this redox substituent as a nucleophilic entity into organic substrates, we generated 2,3-diaryltetrazolinylidenes **16** as novel heterocyclic carbenes in solution (a) by dephosphonionation of a (triphenylphosphonio)tetrazolium salt, (b) via oxidation of a tetrazolium-5-thiolate, and (c) by deprotonation of 2,3-diaryltetrazolium salts. Carbenes **16** were trapped by protonation, deuteronation, halogenation, and oxygen transfer. Generated in the absence of electrophilic trapping agents, carbenes **16** open up to 1-cyanoazimines. The latter show promise as NCN-transfer reagents. The ring opening of carbene **16** is discussed on the basis of semiempirical calculations and compared to such reactions of isomeric tetrazolinylidenes.

The system carbenium ion/radical/carbanion **1**/**2**/**3** represents in principle the simplest two-step redox system of organic chemistry (1). The carbanion center in **1** and the corresponding carbenium



(1)

ion center in **3** exert electronically opposed effects on attached organic groups R. These effects are reversed in the course of redox reaction 1. The obvious preparative benefit to be drawn from this direct redox umpolung[1] is, however, usually thwarted by the fact that for a given set of ligands X, the redox system 1 cannot be reversibly realized due to thermodynamic and/or kinetic instability of certain oxidation levels of the redox system involved. An ideal solution to this problem would consist in coupling the very process of electron transfer with a transformation of carbanion stabilizing substituents X into carbenium ion stabilizing substituents X′ without having to resort to additional external reagents (2). Obviously this abstract postulate could be satisfied by an ECE

† Dedicated to Professor Paul v. R. Schleyer on the occasion of his 60th birthday.

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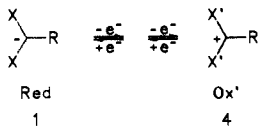


(2)

or EEC sequence[2] in which the chemical step C is an isomerization. All these requirements are in a unique way fulfilled in the classical redox system **5**/**6**,**7**/**8** (Scheme I). In this system oxidation is accompanied by electrocyclic ring closure, whereby substituents X (=π^* acceptors) of **5** are reversibly transformed into substituents X' (lone-pair donors as part of an aromatic ring) of **8**. This transformation structurally requires lone pairs on the terminal nitrogen atoms of **5**. According to ESR investigations this electrocyclization occurs within the Sem intermediate **6** such that the ECE sequence[2] Red–Sem–Sem'–Ox' is followed.[3]

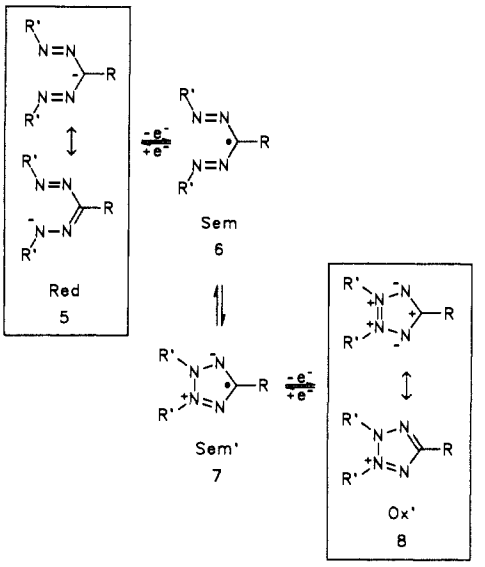
Both formazanide ions **5** and tetrazolium ions **8** represent kinetically and thermodynamically stable systems capable of being isolated for a broad range of substituents.[4] By virtue of these properties the formazanidyl/tetrazoliumyl system could be envisaged as a useful, electronically universal substituent for organic substrates. Synthetic methods that would allow a systematic introduction of this special type of substituent are therefore of particular interest. Isolated reports on S_E reactions[5] at the carbon center of formazanide ions **5** and on S_N reactions at the carbon center of tetrazolium ions[6] **8** or formazans,[7] point to possible approaches to such a development. However, the former type of substitution lacks regioselectivity, and both suffer from a lack of reactivity. In order to circumvent these difficulties, we have pursued as an alternative strategy *nucleophilic* introduction of the tetrazolium system as d^1 synthon[1] into organic substrates. In this context we attempted to generate 2,3-disubstituted tetrazolinylidenes **16** and to trap them by electrophiles.

Tetrazolinylidenes **16** have been postulated as intermediates of base-catalyzed H/D exchange in tetrazolium systems **15**.[8] According to literature reports tetrazolinylidenes **13** and **10**—both isomers of **16**—undergo ring fragmentation to give triazene derivatives[9] **14** and carbodiimides **11** plus dinitrogen[10], respectively (Scheme II). On the basis of these observations, tetrazolinylidene **16** in the absence of trapping agents should open up to the hitherto unknown azimine **17**. Subsequently, we describe generation and trapping experiments of the heterocyclic carbenes **16** including their ring opening to the corresponding azimines. The latter belong to a relatively little investigated class of 1,3-dipoles.[11]

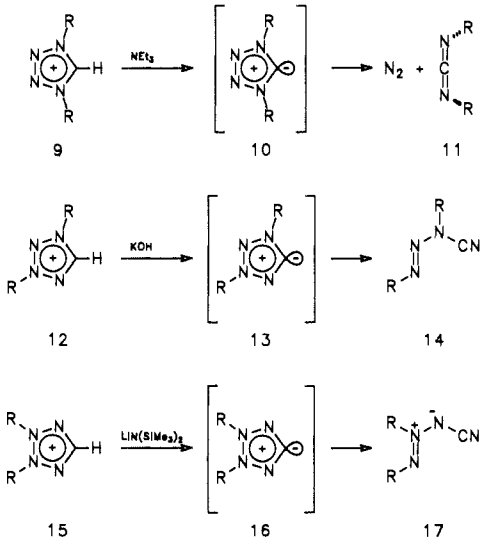
Results and Discussion

Synthesis. Carbenes **16** or corresponding carbenoids have been generated by three different routes: by F^--induced dephosphonionation of dication salt **19** (Scheme III), by oxidation of the mesoionic tetrazolium-5-thiolate **23** (Scheme IV), and by deprotonation of tetrazolium salts **15** (Scheme V). In order to avoid ring-cleavage reactions of tetrazolinylidenes **16** (see below), they were generated either in the presence of an electrophilic trapping reagent or at low temperature.

Scheme I



Scheme II



Generation of Tetrazolinylidenes by F^--Induced Dephosphonionation of 19. On attempted oxidation of ylide **18** with lead tetraacetate, followed by aqueous workup, Märkl isolated triphenylphosphane oxide and the tetrazolium salt **15**.[12] These products can be rationalized by assuming a dication salt of type **19** as an intermediate. We succeeded in synthesizing a first representative of this type of phosphonium salt in high yield by preparative $2e^-$ oxidation of ylide **18** or the corresponding formazan by nitrosyl tetrafluoroborate under anhydrous conditions. When cesium fluoride reacted with dication **19** in the presence of bromine at room temperature, triphenyldifluorophosphane and fluorotetrazolium salt **21** were isolated as products. Salt **21** represents the first example of a 2,3-disubstituted 5-halogenotetrazolium salt. Its extreme sensitivity toward hydrolysis indicates pronounced electrophilicity at the 5-position. Therefore, **21** should be an attractive candidate for nucleophilic functionalization at the 5-position. This will be particularly favorable thermodynamically in combination with silylated nucleophiles.[13]

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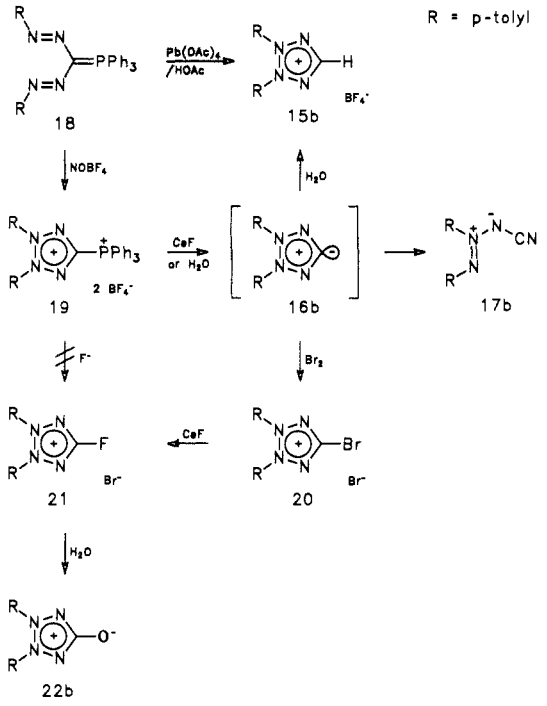
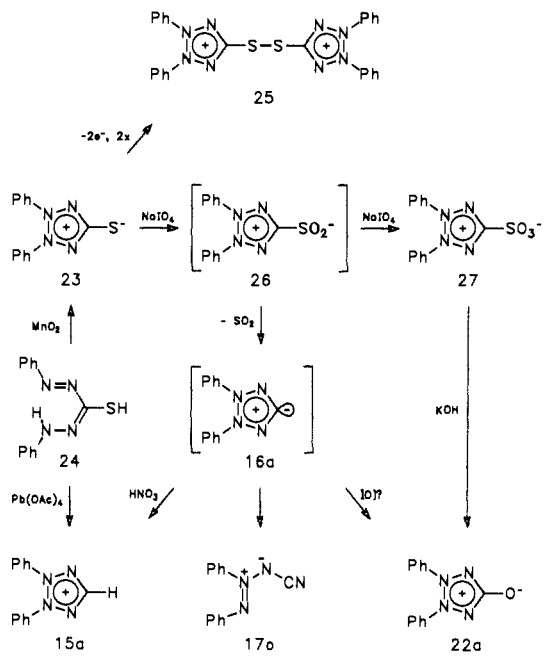
Scheme III



Scheme IV



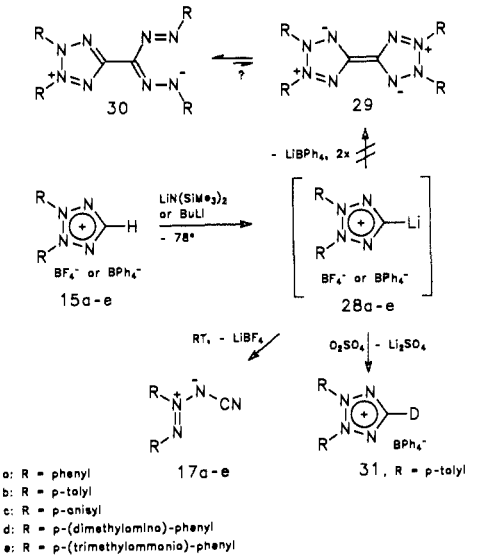
These results can be most reasonably interpreted by assuming a F^--induced dephosphonionation of (triphenylphosphonio)tetrazolium salt **19** to give tetrazolinylidene **16b**. This reactive intermediate is subsequently converted to **20** via bromination followed by F/Br exchange by excess cesium fluoride. In the absence of bromine (or other strong electrophiles) **16b** suffers a ring-opening reaction, which gives the cyanoazimine **17b** as the sole product (see below). These observations together exclude an alternative pathway to **21** involving nucleophilic attack of F^- on the 5-position of tetrazolium salt **19** followed by triphenylphosphane extrusion. As expected on the basis of Märkl's results,[12] hydrolysis of **19** leads quantitatively to the formation of **15b** via **16b** as an intermediate.

Generation of Tetrazolinylidenes by Oxidation of 23. An alternative approach to the generation of tetrazolinylidenes **16** starts from 1,5-diphenylthiocarbazone (**24**) as a commercially available precursor (dithizone). The latter can be oxidized in good yield to 2,3-diphenyltetrazolium-5-thiolate (**23**).[14] On heating a solution of **23** in nitric acid the tetrazolium salt **15a** was isolated in near quantitative yield. Analogous oxidations in the imidazolium and triazolium series had been described by Wanzlick.[15] Using lead tetraacetate as an oxidant, we found that dithizone **24** can be directly converted to **15a**.

If thiolate **23** is oxidized by $KMnO_4$ or $NaIO_4$ in aprotic dipolar solvents (acetonitrile, pyridine, 1,2-dimethoxyethane), the products are the disulfide **25**, the zwitterion **27**, the tetrazolium-5-olate **22a** as well as the azimine **17a** (Scheme IV). From a preparative point of view, the generation of **17a** via this oxidative procedure is less attractive due to the formation of various side products. Nevertheless its generation serves as an indicator for carbene **16a** as an intermediate, which in turn derives from the sulfinate zwitterion **26** by loss of SO_2. Similarly, **26** and **16a** should be precursors of tetrazolium salt **15a** on nitric acid oxidation of thiolate **23**. The formation of **22a** from **26** under the conditions of aprotic oxidation is less easily rationalized. A possible explanation would be direct oxygen atom transfer to **16a** from MnO_4^- or IO_4^-. In any case, **22a** is not produced under the conditions of its generation from the inner sulfonate **27** by adventitious traces of moisture, because potassium hydroxide is required for this transformation. Thiolate **23** behaves analogously to bis(dialkylamino)cyclopropenethiones[16] in that it is converted to disulfide salt **25** by $FeCl_3$ at room temperature and to the tetrazolium-5-sulfonate **27** by *m*-chloroperbenzoic acid at −50 °C.

Generation of Tetrazolinylidenes by Deprotonation of 15. H/D-exchange experiments, performed by Olofson et al.[8,10a] as well as Norris and Henry,[9] demonstrated a dramatic decrease of kinetic CH acidity in going from a 1,4-disubstituted tetrazolium ion **9** via the corresponding 1,3-disubstituted system **12** to the 2,3-disubstituted isomer **15**. In 1973 these results were interpreted on the basis of CNDO/2 calculations.[17] While **9** can be deprotonated by triethylamine and **12** by aqueous KOH, we found that for the deprotonation of **15** strong bases like *n*-butyllithium or lithium hexamethyldisilazide are indeed necessary. Depro-

Scheme V



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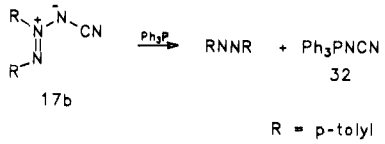
(17) Schroeder, M. A.; Makino, R. C. *Tetrahedron* **1973**, *29*, 3469. We calculated MNDO-based reaction enthalpies for the following acid–base equilibria in the gas phase. (cf. Scheme 1I; R = H): **9** + **13** → **10** + **12**, −21.3 kcal mol^{-1}; **9** + **16** → **10** + **15**, −34.5 kcal mol^{-1}. Both values differ by less than 2 kcal mol^{-1} from the corresponding AM1 energies and from Schroeder's CNDO/2 results.

tonation of the insoluble tetrafluoroborates **15** had to be carried out at about −78 °C in THF in a heterogeneous fashion. After warming to room temperature, the corresponding cyanoazimines **17** were isolated in 60–90% yield. With tetraphenylborate as a counteranion, **15b** can be deprotonated in homogeneous solution even at low temperature with *n*-butyllithium as a base. A dark brown solution was obtained, which was completely and instantaneously decolorized by D_2SO_4. From this solution a mixture of deuterated product **31** (80%) and educt **15b** (20%) could be isolated as tetraphenylborate. This deuteration experiment points to the intermediacy of a carbenoid of type **28** (or oligomers thereof) with considerable longevity. In particular, no ring opening to the corresponding cyanoazimine was observed under these conditions. Ongoing work is concerned with further electrophilic trapping experiments of species **28**.

It is noteworthy that dimerization of species **28** under loss of Li^+ to give **29** is not observed. For R = phenyl, the formal dimer is known from Neugebauer's work to exist as a stable valence isomer of structure **30**.[18] Obviously the ring opening to azimines **17** is more favorable.

Cyanoazimines. Tetrazolinylidenes **16** or **28**, generated under various reaction conditions, can be trapped by sufficiently strong electrophiles. When generated in the absence of electrophiles according to one of the methods described above, 1-cyanoazimines **17** were obtained after workup at room temperature. Structural assignment follows from spectroscopic and analytical data. ^1H NMR spectra are indicative of two nonequivalent aryl moieties. In each of these systems the most intense infrared absorption (ν = 2145–2170 cm^{-1}) can be attributed to the ν(CN) vibration of an electron-rich nitrile unit. Mass spectra of systems **17** show the molecular ions and the ions of the corresponding azoarenes. UV spectra are similar to those of structurally analogous azoxyarenes.[19]

The 1-cyano-2,3-diarylazimines **17** should in the course of the ring-opening reaction be generated in a 1*Z*,2*E* configuration (cf. Discussion). According to chromatographic and ^1H NMR spectroscopic analyses, they seem either to exist in only one out of four possible configurations or to isomerize rapidly at room temperature. Difference NOE experiments can best be reconciled with a 2*Z* configuration, which points to thermodynamic control under the reaction conditions.



The main access to open-chain azimines has almost exclusively been nitrene addition to azo compounds.[20] By contrast, cyanoazimines **17** can be used as cyanonitrene transfer reagents themselves. Azimine **17b** for instance reacted with triphenylphosphane in dichlorobenzene (160 °C, 30 min) under formation of azotoluene and triphenylphosphane *N*-cyanimide **32** (65%).

Ring-Opening Reactions of Isomeric Tetrazolinylidenes. Ring opening of tetrazolinylidene **16** is obviously mechanistically related to the ring opening of **13**. Both can best be described as the final step of an intramolecular E_{1cB} elimination.[21] This type of base-induced ring opening has also been observed with *N*-organyl tetrazoles,[22] triazolium systems,[23] and a number of other five-membered heterocyclic rings.[24] The process can be compared to the isoelectronic isomerization of 1*H*-tetrazoles to the corresponding azidoazomethines, which has been classified as 1,5-dipolar ring opening in thorough theoretical investigations.[25] Similarly, fragmentation of carbene **10** into dinitrogen and carbodiimide **11** could be initiated by stretching one of the two NN bonds to be broken. This would result in a two-stage process[26] with an unsymmetrical transition state of biradicaloid or zwitterionic character. However, synchronous cheletropic fragmentation has to be considered a very likely alternative. According to preliminary calculations, this competition is a very close issue and the calculated activation energy for both alternatives is of an order comparable to those of the ring openings of carbenes **13** and **16**.[27] From this we draw the qualitative conclusion that carbenes **10** and **13** probably could also be trapped at low temperature.

Experimental Section

General Procedures. Melting points were measured on a hot-stage apparatus and are uncorrected. Elemental analysis were determined with a Heraeus CHN-Rapid. UV spectra were recorded on a Beckman DU-8. Infrared spectra were determined on Beckman spectrometers; absorptions are reported in reciprocal centimeters. ^1H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded on JEOL PMX 60, JEOL PS 100, JEOL JNM-GX 400, and JEOL JNM-GX 270 spectrometers. Tetramethylsilane, phosphoric acid, or fluorobenzene were used as standard. Mass spectra were obtained on a Varian MAT CH 4 and a Varian MAT 311 A, using electron impact ionization at 70 eV. Kieselgel 60 (230–400 mesh) silica gel (Merck) was used for column chromatography. All aprotic solvents were dried and operations with them were carried out under N_2 atmosphere.

2,3-Di-*p*-tolyl-5-(triphenylphosphonio)tetrazolium Bis(tetrafluoroborate) (19). Nitrosyl tetrafluoroborate (9.5 g, 81 mmol) was suspended in a solution of 1,5-di-*p*-tolyl-3-(triphenylphosphonio)formazan tetrafluoroborate[12] (23.8 g, 39.6 mmol) in 1,2-dichloroethane (150 mL). After 6 h of refluxing, the excess nitrosyl tetrafluoroborate was filtered off and the solvent was evaporated under vacuum. The brown viscous residue was dissolved in dichloromethane (40 mL) and treated with diethyl ether (10 mL). The crystals that separated out were isolated and washed with ether. Recrystallization from dichloromethane/ether gave light yellow needles of phosphonium salt **19**: 21.9 g, 80%, mp 227 °C dec; IR (Nujol) 1600 (m), 1500 (s), 1440 (vs), 1192 (m), 1175 (s), 1150–950 (vs, br), 827 (s), 730 (s), 687 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 2.39 (6 H, s), 7.30 (4 H, d, J = 8 Hz), 7.82 (10 H, m), 7.95 (5 H, m), 7.93 (4 H, d, J = 8 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.30 (q, J(CH) = 24 Hz), 112.82 (d, J(CP) = 93 Hz), 126.44 (d, J(CH) = 63 Hz), 130.50, 131.08, 135.05 (dd, J(CH) = 64 Hz, J(CP) = 12 Hz), 135.97 (d, J(CH) = 108 Hz), 145.43 (s), 155.16 (d, J(CP) = 130 Hz); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ −15.79; MS, m/z 367 (rel intensity) (2, $ArNPPh_3$), 300 (6, Ph_3PF_2), 281 (9, Ph_3PF), 262 (10, Ph_3P), 250 (22, Ar_2N_2NCN), 235 (16, $Ar_2N_2NCN - CH_3$), 223 (19, Ph_2PF_2), 222 (0.8, Ar_2NCN), 210 (11, Ar_2N_2), 204 (100, Ph_2PF), 154 (11, Ph_2), 127 (10, PhPF), 119 (16, ArN_2), 91 (40, Ar). Anal. Calcd for $C_{33}H_{29}N_4PB_2F_8$: C, 57.76; H, 4.26; N, 8.17. Found: C, 57.78; H, 4.41; N, 8.19.

2,3-Di-*p*-tolyl-5-fluorotetrazolium Bromide (21). Cesium fluoride (0.80 g, 5.3 mmol) was suspended in a solution of the salt **19** (0.89 g, 1.29 mmol) and bromine (0.67 ml, 13 mmol) in dichloromethane (10 mL). After 4 days the insoluble salts were filtered off, washed with dichloromethane (3 × 2 mL) and extracted with freshly distilled thionyl chloride (4 × 3 mL). The clear extraction liquid was evaporated in vacuo and the resulting white greasy residue was taken up in trichloromethane (ca. 4 mL). After some days the light yellow product **21**, which still contained 1 mol of thionyl chloride, crystallized from the supersaturated solution: 0.44 g, 73%; mp 110 °C; IR (Nujol) 1591 (vs), 1500 (m), 1361 (w), 1150

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(27) We calculated the following energies (kcal mol^{-1}) for the ring-opening reactions of tetrazolinylidenes **10**, **13**, and **16** (cf. Scheme 11; R = H), by using the AM1 method and a 100 × 100 configuration interaction: reaction enthalpy −71.1, −59.6, −99.9, and activation energy 23.5, 23.0, 29.0, for **16**, **13**, and **10**, respectively. The activation energy for the synchronous cheletropic fragmentation of **13** was found to be 1 kcal mol^{-1} less favorable than the activation energy for asynchronous ring opening.

(w), 995 (w), 819 (s), 738 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (6 H, s), 7.31 (4 H, d, J = 8 Hz), 7.78 (4 H, d, J = 8 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.56, 126.16, 130.36, 130.79, 145.72, 167.13 (d, J(CF) = 255 Hz); ^{19}F NMR (254 MHz, $CDCl_3$) δ −116.77; MS, m/z 269 (rel intensity) (100, M^+), 119 (10, ArN_2), 105 (10, ArN), 91 (72, Ar). Anal. Calcd for $C_{15}H_{14}N_4FBr{\cdot}SOCl_2$: C, 38.48; H, 3.01; N, 11.97. Found: C, 37.95; H, 3.09; N, 11.48. The fluorotetrazolium salt **21** could be hydrolyzed to a mixture of colorless 2,3-di-*p*-tolyl-tetrazolium-5-olate **22b** and protonated **22b** by solving it in wet acetone or hot water: IR (Nujol) 3050 (w), 2730 (w), 2643 (w), 2550 (w), 2460 (w), 2380 (w), 1585 (vs), 1503 (s), 995 (w), 830 (s); ^{1}H NMR (60 MHz; DMSO-d_6) δ 2.30 (6 H, s), 7.31 (4 H, d, J = 9 Hz), 7.54 (4 H, d, J = 9 Hz); MS, m/z 266 (rel intensity) (100, M^+), 238 (26, Ar_2N_2CO), 210 (4, Ar_2N_2), 182 (10, Ar_2), 119 (ArN_2). The spectra were identical with those obtained from authentic material.[7a]

Reaction of the Phosphonium Salt 19 with Cesium Fluoride. Cesium fluoride (0.68 g, 4.5 mmol) was suspended in a solution of the salt **19** (1.12 g; 1.63 mmol) in dichloromethane (10 mL). After 1 week the cesium salts were filtered off and washed with dichloromethane (4 × 3 mL). The combined filtrates were concentrated and treated with ether. The azimine **17b** precipitated. Further addition of ether yielded crystalline triphenyldifluorophosphane. Both precipitates were recrystallized from dichloromethane/ether. **17b**: yellow needles, 0.26 g, 64%; mp 177 °C dec; UV (CH_3CN) 366 nm (ϵ = 2.11 × 10^4 dm^3 mol^{-1} cm^{-1}); IR (KBr) 3061 (w), 2920 (w), 2161 (vs), 1604 (m), 1503 (m), 1456 (s), 1317 (m), 1297 (m), 1268 (s), 1211 (m), 1183 (m), 1174 (m), 1018 (w), 837 (w), 820 (s), 811 (m), 655 (w), 533 (m), 514 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (3 H, s), 2.46 (3 H, s), 7.32 (2 H, d, J = 9 Hz), 7.36 (2 H, d, J = 9 Hz), 7.58 (2 H, d, J = 9 Hz), 8.13 (2 H, d, J = 9 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.38, 21.72, 114.77, 123.19, 127.23, 129.44, 129.96, 142.56, 142.70, 144.74; MS m/z 250 (rel intensity) (74, M^+), 235 (43, $M^+ - CH_3$), 222 (3, Ar_2NCN), 210 (60, Ar_2N_2), 119 (72, ArN_2), 105 (9, ArN), 91 (100, Ar). Anal. Calcd for $C_{15}H_{14}N_4$: C, 71.97; H, 5.64; N, 22.38. Found: C, 71.75; H, 5.66; H, 22.87. **Triphenyldifluorophosphane**: colorless needles, 0.24 g, 49%; mp 154–156 °C dec; IR (Nujol) 3070 (w), 3055 (w), 1586 (w), 1482 (m), 1438 (s), 1113 (vs), 760 (m), 745 (m), 725 (s), 690 (m), 670 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (11 H, m), 8.00 (2 H, dd, J = 16, 1.5 Hz), 8.02 (2 H, dd, J = 15, 1.5 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 128.01, 128.18, 128.63, 128.75, 128.98, 129.18, 130.25, 131.10, 131.14, 131.88, 131.97, 132.70, 133.50, 133.62; ^{31}P NMR (40.5 MHz, $CDCl_3$) δ 54.60 (t, $J(PF_2)$ = 659 Hz); MS, m/z 300 (rel intensity) (3, M^+), 281 (3, Ph_3PF), 262 (3, Ph_3P), 223 (8, Ph_2PF_2), 204 (100, Ph_2PF), 154 (12 Ph_2), 127 (11, PhPF), 77 (12, Ph). Anal. Calcd for $C_{18}H_{15}PF_2$: C, 72.00; H, 5.04. Found: C, 72.07; H, 5.06.

1-Cyano-2,3-di-p-tolylazimine (17b) by Deprotonation of 2,3-Di-*p*-tolyltetrazolium Tetrafluoroborate (15b). A solution of lithium hexamethyldisilazide (1.74 g, 10.4 mmol) in tetrahydrofuran (10 mL) was added dropwise at −78 °C to a stirred suspension of the tetrazolium salt **15b** (3.56 g, 10.5 mmol) in tetrahydrofuran (60 mL). After 2 h of stirring and warming to room temperature, excess tetrazolium salt was filtered off and the yellow-brown solution was concentrated and treated with ether. Washing of the precipitated yellow powder with ether and its recrystallization from dichloromethane/ether yielded bright yellow needles of azimine **17b**: 1.84 g, 70%. Anal. Calcd for $C_{15}H_{14}N_4$: C, 71.97; H, 5.64; N, 22.38. Found: C, 71.50; H, 5.50; N, 21.79.

2,3-Di-*p*-anisyltetrazolium Tetrafluoroborate (15c). The pale yellow tetrazolium salt **15c** was prepared by the method of Märkl:[12] mp 160–161 °C; IR (KBr) 1600 (m), 1505 (s), 1260 (s), 1116 (s), 1073 (vs), 827 (m); ^{1}H NMR (400 MHz, CD_3CN) δ 3.87 (6 H, s), 7.11 (4 H, d, J = 9 Hz), 7.57 (4 H, d, J = 9 Hz), 9.53 (1 H, s); ^{13}C NMR (100.5 MHz, CD_3CN) δ 56.95, 116.46, 118.44, 126.32, 128.73, 154.72, 164.55; MS, m/z 284 (rel intensity) (20, $M^+ + H$), 242 (44, Ar_2N_2), 214 (23, Ar_2), 135 (90, ArN_2), 122 (93, ArNH), 107 (100, Ar). Anal. Calcd for $C_{15}H_{15}N_4O_2BF_4$: C, 48.68; H, 4.09; N, 15.14. Found: C, 48.56; H, 4.11; N, 15.15.

1-Cyano-2,3-di-*p*-anisylazimine (17c). The azimine **17c** was prepared by the method described above for **17b**: yellow needles, 0.83g; 66%; mp 136 °C dec; UV (CH_3CN) 377 nm (ϵ = 1.5 × 10^4 dm^3 mol^{-1} cm^{-1}); IR (KBr) 2149 (v), 1592 (vs), 1496 (m), 1246 (vs), 1160 (s), 1020 (m), 824 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (3 H, s), 3.91 (3 H, s), 7.01 (2 H, d, J = 9 Hz), 7.02 (2 H, d, J = 9 Hz), 7.66 (2 H, d, J = 9 Hz), 8.32 (2 H, d, J = 9 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 55.55, 55.61, 113.81, 114.14, 115.28, 124.97, 129.98, 138.76, 139.95, 161.67; MS, m/z 282 (rel intensity) (14, M^+), 267 (10, $M^+ - CH_3$), 242 (100, Ar_2N_2), 135 (94, ArN_2), 121 (13, ArN), 107 (84, Ar). Anal. Calcd for $C_{15}H_{14}N_4$: C, 63.82; H, 5.00; N, 19.85. Found: C, 63.43; H, 5.08; N, 19.61.

1-Cyano-2,3-bis[*p*-(dimethylamino)phenyl]azimine (17d). A solution of lithium hexamethyldisilazide (0.158 g, 0.94 mmol) in tetrahydrofuran (5 mL) was added dropwise at −78 °C to a stirred suspension of the tetrazolium salt **15d**[12] (0.396 g, 1.00 mmol) in tetrahydrofuran (30 mL). After 2 h of stirring the brown suspension was allowed to warm to room temperature. The excess tetrazolium salt was filtered off and washed with tetrahydrofuran. The combined filtrates were concentrated and chromatographed on silica gel [dichloromethane/ether (1:1) as eluant; a purple band was collected]. Recrystallization from dichloromethane/ether gave red-brown crystals of azimine **17d**: 0.182 g, 63%; soluble in weakly acid water with intense eosin red color; mp 195–198 °C dec; UV (CH_3CN) 463 nm (ϵ = 4.1 × 10^4 dm^3 mol^{-1} cm^{-1}); IR (Nujol) 2146 (vs), 1596 (vs), 1518 (s), 1369 (s), 1232 (m), 1169 (vs), 944 (w), 822 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.03 (6 H, s), 3.10 (6 H, s), 6.69 (4 H, d, J = 10 Hz), 7.59 (2 H, d, J = 9 Hz), 8.31 (2 H, d, J = 10 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 40.03, 40.19, 110.69, 110.90, 117.34, 124.66, 130.39, 135.49, 135.92, 151.614, 151.75; MS, m/z 308 (rel intensity) (20, M^+), 268 (86, Ar_2N_2), 148 (5, ArN_2), 134 (44, ArN), 120 (100, Ar), 105 (16, Ar − Me), 91 (9, PhNH), 77 (17, Ph). Anal. Calcd for $C_{17}H_{20}N_6$: C, 66.21; H, 6.54; N, 27.25. Found: C, 66.26; H, 6.57; N, 27.17.

2,3-Bis[*p*-(trimethylammonio)phenyl]tetrazolium Tris(tetrafluoroborate) (15e). Trimethyloxonium tetrafluoroborate (0.88 g, 5.9 mmol) and the yellow tetrazolium tetrafluoroborate **15d**[12] (0.84 g, 2.1 mmol) were suspended in dichloromethane (50 mL). After 1 day the colorless, insoluble tetrazolium tris(tetrafluoroborate) **15e** was filtered off and recrystallized from acetonitrile/dichloromethane: 0.82 g, 65%; mp dec >300 °C; IR (Nujol) 3130 (w), 1503 (s), 1298 (m), 990–1150 (vs), 847 (s); ^{1}H NMR (400 MHz, CD_3NO_2) δ 3.80 (18 H, s), 8.06 (4 H, d, J = 9.5 Hz), 8.24 (4 H, d, J = 9.5 Hz), 9.79 (1 H, s); ^{13}C NMR (100.5 MHz, CD_3NO_2) δ 58.79, 125.01, 129.68, 135.16, 152.25, 156.50. Anal. Calcd for $C_{19}H_{27}N_6B_3F_{12}$: C, 38.04; H, 4.54; N, 14.01. Found: C, 37.78; H, 4.61; N, 14.02. By solving the tetrazolium tris(tetrafluoroborate) **15e** in water, adding a solution of sodium tetraphenylborate, and recrystallizing the dried precipitate from THF it was converted into the tetraphenylborate **15e**.

1-Cyano-2,3-bis[*p*-(trimethylammonio)phenyl]azimine Bis(tetraphenylborate) (17e). Lithium hexamethyldisilazide (35 mg, 0.21 mmol) dissolved in tetrahydrofuran (2 mL) was added at −100 °C to a solution of the tetrazolium tetraphenylborate **15e** (0.30 g, 0.23 mmol) in tetrahydrofuran (40 mL). After 2 h of stirring and warming to room temperature the precipitated pale yellow **17e** was filtered off and recrystallized from acetonitrile or DMSO/*t*-BuOH: 0.19 g, 85%; mp dec >280 °C (CH_3CN); UV (CH_3CN) 355 nm (ϵ = 9.6 × 10^3 dm^3 mol^{-1} cm^{-1}); IR (KBr) 2170 (s), 1624 (s), 1480 (vs), 844 (m), 735 (s), 710 (vs); ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.60 (9 H), 3.65 (9 H), 6.79 (8 H, t, J = 7.3 Hz), 6.93 (16 H, t, J = 7.3 Hz), 7.19 (16 H, m), 8.08 (2 H, d, J = 9.7 Hz), 8.14 (2 H, d, J = 9.5 Hz), 8.27 (2 H, d, J = 9.2 Hz), 8.31 (2 H, d, J = 9.5 Hz); ^{13}C NMR (100.5 MHz, DMSO-d_6) δ 56.41, 56.55, 113.19, 117.96, 121.48, 121.54, 122.73, 125.25, 125.28, 125.72, 126.08, 135.49, 144.98, 146.65, 149.17, 163.33 (q, J = 49 Hz). Anal. Calcd for $C_{67}H_{66}N_6B{\cdot}^3/_2(H_6C_2SO)$: C, 76.84; H, 6.91; N, 7.68. Found: C, 77.16; H, 6.83; N, 7.65.

2,3-Diphenyltetrazolium Tetrafluoroborate (15a) by Oxidation of 2,3-Diphenyltetrazolium-5-thiolate (23). 2,3-Diphenyltetrazolium-5-thiolate[14] (**23**; 0.254 g, 1.00 mmol) was carefully added to 3.0 mL of 36% nitric acid. The reaction mixture was warmed at 100 °C for 2 h. Tetrafluoroboric acid (0.25 mL of a 50% aqueous solution, 2.0 mmol) was added and the solvent removed in vacuo. The white residue was recrystallized from methanol and ether to afford colorless crystals of **15a**: 0.294 g; 95%; mp 217 °C; IR (KBr) 1479 (s), 1290 (s), 1140–1020 (vs), 760 (s), 675 (s); ^{1}H NMR (60 MHz, CD_3CN) δ 7.71 (10 H, m), 9.67 (1 H, s); ^{13}C NMR (25 MHz, CD_3CN) δ 118.31, 126.92, 131.50, 135.23, 155.10 (d, J = 96 Hz). Anal. Calcd for $C_{13}H_{11}N_4BF_4$: C, 50.36; H, 3.58; N, 18.07. Found: C, 50.03; H, 3.87; N, 17.97.

2,3-Diphenyltetrazolium Tetrafluoroborate (15a) by Oxidation of Dithizone (24). A suspension of dithizone (6.4 g, 25 mmol) in dichloromethane (200 mL) was added to a dichloromethane solution (200 mL) of lead tetraacetate (46 g, 0.1 mol) at −10 °C. The reaction mixture was extracted with water. Hydrofluoric acid (3.8 mL of a 50% aqueous solution, 0.11 mol) was added to the aqueous extracts and the precipitated lead fluoride was removed by centrifugation. The product **15a** was precipitated by addition of tetrafluoroboric acid (4.1 mL of a 50% aqueous solution, 30 mmol) and recrystallized from methanol: 5.05 g; 65%. Anal. Calcd for $C_{13}H_{11}N_4BF_4$: C, 50.36; H, 3.58; N, 18.07. Found: C, 50.14; H, 3.62; N, 17.87.

1-Cyano-2,3-diphenylazimine (17a). The azimine **17a** was prepared from the corresponding tetrazolium tetrafluoroborate **15a** by the method described above for the azimine **17b**: yellow needles, 0.40 g; 68%; mp 92 °C; UV (CH_3CN) 357 nm (ϵ = 1.49 × 10^4 dm^3 mol^{-1} cm^{-1}); IR (KBr) 2145 (vs), 1457 (s), 1432 (m), 1260 (s), 755 (vs), 682 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.70 (8 H, m), 8.17 (2 H, d, J = 8 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 114.20, 123.30, 126.83, 128.81,

129.57, 131.36, 131.96, 144.64, 146.90; MS, m/z 222 (rel intensity) (32, M^+), 221 (62, $M^+ - H$), 182 (100, Ph_2N_2), 152 (60, $H_4C_6C_6H_4$), 105 (63, PhN_2), 77 (54, Ph). Anal. Calcd for $C_{13}H_{10}N_4$: C, 70.26; H, 4.54; N, 25.21. Found: C, 70.36; H, 4.58; N, 25.35.

1-Cyano-2,3-diphenylazimine (17a) by Oxidation of 2,3-Diphenyltetrazolium-5-thiolate (23). Sodium periodate (2.14 g, 10.0 mmol) was suspended in a solution of 2,3-diphenyltetrazolium-5-thiolate[14] (**23**; 0.253 g, 0.99 mmol) in acetonitrile (10 mL). After 2 days the sodium salts and the tetrazolium-5-sulfonate **27** were filtered off and washed with dichloromethane (2 × 10 mL). The solvent of the combined filtrates was removed in vacuo. The residue was extracted with dichloromethane and the remaining dithiobis(2,3-diphenyltetrazolium) bis(periodate) (**25**) was filtered off. The solution was chromatographed on a 3-cm column packed with a 2-cm bed of silica gel, employing dichloromethane/ether (1:1) as eluant for the azimine **17a** and trichloromethane/methanol (9:1) as eluant for the tetrazolium-5-olate **22a**. Both were recrystallized from dichloromethane/ether. The periodate **25** was dissolved in methanol. The tetrafluoroborate precipitating from the solution after the addition of tetrafluoroboric acid was recrystallized from methanol/ether. The sodium salts containing the tetrazolium-5-sulfonate **27** were dissolved in 10 mL of water and acidified with 0.5 mL of sulfuric acid. The tetrazolium-5-sulfonate was extracted from this solution with dichloromethane and recrystallized from acetonitrile. **17a**: 20.4 mg, 9.2%. Anal. Calcd for $C_{13}H_{10}N_4$: C, 70.26; H, 4.54; N, 25.21. Found: C, 69.95; H, 4.66; N, 24.82. The infrared and mass spectra were identical with those obtained from the azimine **17a** prepared by deprotonation of 2,3-diphenyltetrazolium tetrafluoroborate. **22a**: colorless, rhombic crystals, 20 mg, 8.5%; mp 179 °C (explodes); IR (KBr) 1665 (vs), 1640 (s), 1590 (m), 1490 (s), 767 (m); ^{1}H NMR (60 MHz, D_3COD) δ 7.60 (m); MS, m/z 238 (rel intensity) (42, M^+), 210 (32, Ph_2N_2CO), 168 (12, Ph_2N), 154 (13, Ph_2), 105 (76, PhN_2), 77 (100, Ph). Anal. Calcd for $C_{13}H_{10}N_4O \cdot {}^1/_8(CH_2Cl_2)$: C, 63.35; H, 4.15; N, 22.51. Found: C, 63.37; H, 4.22; N, 22.45. **25**: colorless crystals, 87 mg, 26%; mp 155–157 °C; IR (KBr) 1480 (m), 1355 (m), 1119 (vs), 1075 (vs), 1058 (s), 993 (m), 760 (m), 680 (m); ^{1}H NMR (400 MHz, CD_3CN) δ 7.7 (m); ^{13}C NMR (100.6 MHz, CD_3CN) δ 127.41, 131.95, 134.48 135.86, 168.03; MS, m/z 254 (rel intensity) (100, ${}^1/_2$ M^+), 226 (51, ${}^1/_2$ $M^+ - N_2$), 167 (28), 152 (32), 105 (55, PhN_2), 91 (26, PhN), 77 (48, Ph). Anal. Calcd for $C_{26}H_{20}N_8S_2B_2F_8$: C, 45.77; H, 2.96; N, 16.43. Found: C, 45.26; H, 2.96; N, 16.13. A pure sample of **25** was prepared by oxidation of **23** with excess $FeCl_3$ in ethanol at room temperature.[28] **27**: colorless needles, 61 mg, 20%; mp dec >360 °C (explodes); IR (KBr) 1484 (m), 1466 (w), 1310 (w), 1275 (vs), 1250 (vs), 1158 (m), 1057 (vs), 1012 (m), 994 (w), 774 (w), 757 (m), 681 (m), 640 (s); ^{1}H NMR (400 MHz, CD_3CN) δ 7.7 (m); ^{13}C NMR (100.6 MHz, CD_3CN) δ 127.06, 131.46, 134.04, 135.16. Anal. Calcd for $C_{13}H_{10}N_4O_3S$: C, 51.65; H, 3.33; N, 18.53; S, 10.61. Found: C, 51.45; H, 3.42; N, 18.31; S, 10.55. A pure sample of **27** was prepared by oxidation of **23** with excess *m*-chloroperbenzoic acid at −50 °C.[28]

(28) Reaction conditions for these oxidations were essentially the same as reported for the oxidation of bis(dialkylamino)cyclopropenethiones.[16]

2,3-Di-*p*-tolyl-5-deuteriotetrazolium Tetraphenylborate (31). A solution of *n*-butyllithium in hexane (1.00 mL of a commercially available 1.6 M solution, 1.6 mmol) was added dropwise at −78 °C to a stirred pale yellow solution of the tetrazolium tetraphenylborate **15b** (0.594 g, 1.04 mmol) in tetrahydrofuran (20 mL). The dark brown solution was titrated with deuteriosulfuric acid (0.1 g of D_2SO_4 mixed with 2 mL of tetrahydrofuran at −78 °C) until the color changed to pale yellow. An excess of acid causes blackening of the solution. After being warmed to room temperature, the solution was treated with ether. Subsequent washing of the precipitate with ether and recrystallization from tetrahydrofuran/ether furnished yellow crystals of the tetrazolium salt **31**: 0.37 g, 62%; mp 181–183 °C dec; IR (KBr) 3050 (s), 2340 (w), 1600 (m), 1580 (m), 1427 (m), 1295 (s), 815 (s), 805 (s), 725 (s), 700 (vs), 610 (s); ^{1}H NMR (400 MHz, D_3CCN) δ 2.39 (6 H, s), 6.83 (4 H, t, J = 7 Hz), 6.98 (8 H, dd, J = 8, 7 Hz), 7.28 (8 H, m), 7.37 (4 H, d, J = 9 Hz), 7.46 (4 H, d, J = 9 Hz), 9.38 (0.2 H, s); ^{13}C NMR (100.5 MHz, D_3CCN) δ 154.62 (t, J = 35.1 Hz). Anal. Calcd for $C_{39}H_{34}DN_4B \cdot CH_3CN$: C, 80.39; H, 6.42; N, 11.43. Found: C, 80.14; H,D, 6.22; N, 11.36.

Reaction of Azimine 17b with Triphenylphosphane. 1-Cyano-2,3-di-*p*-tolylazimine (**17b**; 0.251 g, 1.00 mmol) and triphenylphosphane (0.393 g, 1.50 mmol) were dissolved in 1,2-dichlorobenzene (8.0 mL) at ca. 160 °C. After 30 min of heating the solvent was removed in vacuo and the residue was chromatographed on silica gel (benzene as eluant for the yellowish-orange azotoluene; ethyl acetate as eluant for the colorless cyanimide **32**). Recrystallization of the yellowish-orange fraction from pentane and sublimation gave orange needles of azotoluene (0.128 g, 61%). The cyanimide **32** was partly hydrolyzed during the chromatography. Recrystallization from ether/pentane yielded colorless crystals of triphenylphosphane *N*-cyanimide **32** (0.196 g; 65%), contaminated by triphenylphosphane oxide. **Azotoluene**: mp 139–141 °C; IR (Nujol) 1602 (m), 1598 (m), 1156 (s), 827 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (6 H, s), 7.30 (4 H, d, J = 8 Hz), 7.81 (4 H, d, J = 8 Hz); MS, m/z 210 (rel intensity) (66, M^+), 119 (50, ArN_2), 105 (5, ArN), 91 (100, Ar). Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 80.19; H, 6.93; N, 13.24. **32**: mp 188–190 °C; IR (Nujol) 2190 (vs), 1465 (vs), 1440 (s), 1380 (m), 1120 (s), 728 (m), 698 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (m); MS, m/z 302 (rel intensity) (100, M^+), 262 (12, Ph_3P), 183 (18, $PC_{12}H_8$), 77 (5, Ph); HRMS (M^+) calcd for $C_{19}H_{15}N_2P$ 302.09728, found 302.09714; ($M^+ - H$) calcd for $C_{19}H_{14}N_2P$ 301.08946, found 301.08957.

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Registry No. 15a, 1495-97-2; **15b**, 123903-35-5; **15c**, 123903-36-6; **15d**, 3888-52-6; **15e**, 123903-43-5; **17a**, 123903-41-3; **17b**, 123903-34-4; **17c**, 123903-37-7; **17d**, 123903-38-8; **17e**, 123903-40-2; **18**·BF_4, 123903-29-7; **19**, 123903-31-1; **21**, 123903-32-2; **22a**, 6888-71-7; **22b** 5-olate derivative, 55667-67-9; **22b** protonated derivative, 123903-33-3; **23**, 11065-31-9; **24**, 60-10-6; **25**, 123933-24-4; **27**, 123903-44-6; **31**, 123903-46-8; **32**, 4027-82-1; Ph_3PF_2, 845-64-7.