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REACTIONS OF TRIMETHYLSILYL AZIDE WITH ALDEHYDES: FACILE AND CONVENIENT SYNTHESES OF DIAZIDES, TETRAZOLES, AND NITRILES

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Abstract: The reactions of trimethylsilyl azide (TMSA) with various aldehydes were found to be versatile procedures for the synthesis of *gem*- and 1,3-diazides, tetrazoles, and nitriles, whose formation was varied by controlling the quantities of TMSA, catalyst, and the reaction conditions.

Introduction

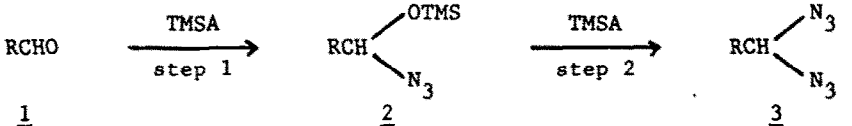
A great deal of attention has been focused on silicon compounds carrying a functional group (halo, cyano, alkylthio, *etc.*) because these compounds play important roles in organic synthesis.[1] Of these, it has been shown that silyl cyanide and silyl thioether were highly versatile reagents for converting carbonyl compounds into 1:1-adducts,[1,2,3] whereas silyl azides reacted only with aliphatic aldehydes to give *α*-siloxy azide.[4] In contrast to the reported studies,[3,5] we have shown that the reactions of trimethylsilyl azide (TMSA) with ketones gave *gem*-diazidoalkanes and/or 1,5-disubstituted-1*H*-tetrazoles.[6,7] Thus, we reinvestigated the reactivity of TMSA toward various aldehydes and would like to describe the formations of *gem*- and 1,3-diazides, 1-substituted and unexpected 1,5-disubstituted tetrazoles, and nitriles in this paper.

Results and Discussion

Formations of *gem*- and 1,3-Diazides

There has been a few reports on the preparation of *gem*-diazides including our previous paper:[6] namely the nucleophilic substitution of *gem*-dihalides by azide ion[8,9,10] and the addition of hydrazoic acid to C≡C bonds.[11] However, these reactions gave only internal *gem*-diazides and, moreover, the applicabilities of these methods as general synthetic routes to *gem*-diazides are limited due to the inaccessibility of the reagents and other competitive reactions (*e.g.*, 1,3-dipolar addition of hydrazoic acid to unsaturated bonds).

The reaction of 2-methylpropanal (1c) with TMSA (2.3 equiv) in the presence of a catalytic amount of $SnCl_2$ gave 1,1-diazido-2-methylpropane (3c) in a 69% yield. Other aldehydes also gave 3 in a similar manner (eq. 1). The products were confirm-



(eq. 1)

1 2 3

a) R=Et, b) R=*n*-Pr, c) R=*i*-Pr, d) R=*n*-Bu, e) R=*i*-Bu, f) R=*t*-Bu, g) R=Cl_3C, h) R=*n*-C_5H_{11}, i) R=C_6H_5, j) R=*p*-MeC_6H_4, k) R=*p*-$MeOC_6H_4$, l) R=*p*-ClC_6H_4, m) R=*p*-$O_2NC_6H_4$, n) R=*m*-$O_2NC_6H_4$, o) R=*p*-$OHCC_6H_4$, p) R=*p*-$(N_3)_2HCC_6H_4$, q) R=*p*-NCC_6H_4

ed by spectral analysis and by conversion into 1-substituted tetrazoles.[8] The results and their spectral data are summarized in Table 1. Either zinc chloride or trimethylsilyl trifluoromethanesulfonate (TMSOTf) also promoted the reaction between aldehydes with TMSA.

Table 1. Yields of *gem*-Diazidoalkanes (3) and Their ^{1}H NMR, IR, and MS Spectra

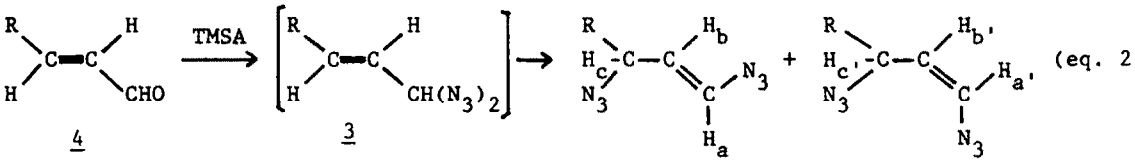
Compd	Yield/%	^{1}H NMR/ppm		IR/cm^{-1}	MS
		$CH(N_3)_2$	others	$\nu(N_3)_2$	*m/z*
3a	72	4.90 (t)	0.98 (t), 1.75 (q)	2100	97 (M^+-Et)
3b	78	4.70 (t)	0.95 (t), 1.45-1.78 (m)	2100	97 (M^+-Pr)
3c	69	4.55 (d)	1.00 (d), 1.90 (m)	2100	97 (M^+-Pr)
3d	58	4.70 (t)	1.00 (t), 1.40-1.90 (m)	2100	97 (M^+-Bu)
3e	62	4.75 (t)	1.00 (d), 1.90 (m)	2100	97 (M^+-Bu)
3f	52[a]	4.40 (s)	0.97 (s)	2100	97 (M^+-Bu)
3i	87	5.60 (s)	7.30 (s)	2100	132 (M^+-N_3)
3j	88	5.58 (s)	2.28 (s), 7.18 (s)	2100	146 (M^+-N_3)
3k	83	5.68 (s)	3.78 (s), 6.95, 7.35 (ABq)	2100	
3l	93	5.55 (s)	7.23 (s)	2100	168 (M^+-N_3)
3m	58	5.75 (s)	7.52, 8.20 (ABq)	2110	
3n	83	5.75 (s)	7.50-8.21 (m)	2110	177 (M^+-N_3)
3p[b]	15	5.70 (s)	7.40 (s)	2100	228 (M^+-N_3)
3q[b]	35	5.80 (s)	7.48, 7.68 (ABq)	2100	157 (M^+-N_3)

a) Compound 2f was also obtained in a 24% yield. b) These compounds were obtained by the reaction of terephthalaldehyde with TMSA at 60 °C.

Except for 2,2-dimethylpropanal (1f) and trichloroethanal (1g), diazides 3 were obtained as the sole product in good to excellent yields. Compound 1f gave siloxy azide 2f (24%) together with diazide 3f (52%), and 1g provided only siloxy azide 2g (56%). The yield of 3m from *p*-nitrobenzaldehyde (1m) was also poorer than those of other aromatic aldehydes. These findings suggest that both of steric and electronic effects seem to be important in not step 1 but also step 2 of equation 1.

Coupled with our proceeding results,[6] this approach offers several advantages for preparing either terminal or internal *gem*-diazides on the following aspects: i) generality of the procedure, ii) neutral and mild conditions, iii) requirement of only commercially available reagents, and iv) few by-products.

On the contrary, the reactions of α,β-unsaturated aldehydes (4a and 4b) with TMSA catalyzed by TMSOTf gave 1,3-diazide 5 as an unseparable mixture of *E* and *Z* isomers (eq. 2). The product yields were determined by ^{1}H NMR spectra. These di-



4

a) R=Me

B) R=*n*-Pr

3

5

a) 38% 23%

b) 40% 29%

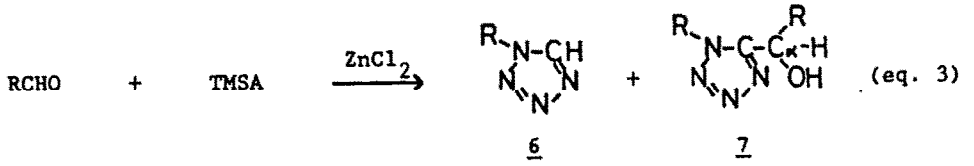
(eq. 2

azides 5 were postulated to arise from *gem*-diazides 3 *via* an allylic rearrangement of an azido group.[12]

Formation of Tetrazole Derivatives

As a method for confirming the structure of *gem*-diazide, we found that $ZnCl_2$ converted the compound into tetrazole derivative at moderate temperature.[6] Thus, this finding led us to examine a direct synthesis of monosubstituted tetrazoles (*e.g.*, 1-substituted-1*H*-tetrazole) from aldehydes and TMSA.

When a mixture of 2-methylpropanal (1c), TMSA (3 equiv), and $ZnCl_2$ (1 equiv) was stirred for 72 h at room temperature, a 45% yield of 1-(1-methylethyl)-1*H*-tetrazole (6c) along with a trace of 5-(1-hydroxy-2-methylpropyl)-1-(1-methylethyl)-1*H*-tetrazole (7c) was isolated. Under the similar conditions, compounds 1a and 1b were converted to the corresponding tetrazoles 6a and 6b in 38 and 78% yields, respectively. No 1,5-disubstituted tetrazoles 7 were observed in the reaction mixture. Similar treatment of *t*-BuCHO (1f) yielded 6f (34%) and 7f (22%). Hexanenitrile (30%) together with 1-pentyl-1*H*-tetrazole (6h, 63%) was found to arise from hexanal (1h) and TMSA.



6 7 (eq. 3)

With an equimolar amount of TMSA, on the other hand, aliphatic aldehydes (1a-c and 1f) were mainly converted to unexpected disubstituted tetrazoles 7. The results are compiled in Table 2. These studies indicate that the selective formation of either tetrazole 6 or 7 can be achieved by varying the quantity of TMSA used.

Table 2. Product Distributions of Reactions between Aliphatic Aldehydes and TMSA

Aldehyde	TMSA (equiv)	Product[a]/% 6	7
1a	1	-	31
	3	38	-
1b	1	-	49
	3	78	-
1c	1	-	45
	3	45	trace
1f	1	7	48
	3	34	22

a) In each case, the corresponding diazide 3 was involved.

Unfortunately, the direct aryl substituted tetrazole synthesis failed because the reactions of aromatic aldehydes with TMSA preferentially produced the corresponding nitriles rather than tetrazoles. A catalytic decomposition of isolated aryldiazidomethanes produced tetrazoles 6 only in a range of 20-50% yields along with nitriles in 30-60% yields.

To account for the tetrazole formation, we assume that imidoyl azide (i), formed from *gem*-diazide by nitrogen evolution and alkyl migration, cyclizes to give monosubstituted tetrazole 6[13] or it reacts with another aldehyde molecule to give disubstituted tetrazole 7. Tetrazole 7 was not obtained by the treatment of 6 with aldehyde under the reaction conditions which produced 7, and the reaction of 3c with *t*-BuCHO and $ZnCl_2$ gave 5-(1-hydroxy-2,2-dimethylpropyl)-1-(1-methylethyl)-1*H*-tetrazole[14] in a 28% yield together with the starting material 3c and tetrazole 6c. These findings and the product distributions shown in Table 2 bring out the following assumption. When an equimolar amount of TMSA was employed, an initially formed 2 further reacts with TMSA much more rapidly to generate 3, which then reacts with

an aldehyde to give tetrazole 7 as the major product. With a three-fold excess of TMSA, the aldehyde was completely converted into diazide 3, which then led to tetrazole 6 as the major product. With sterically hindered aldehydes (1e and 1f), tetrazole 7 was also obtained as a by-product even when a three-fold excess of TMSA was used. This is rationalized by considering that such bulky substituent retards both of steps 1 and 2 of equation 1 and, in these cases, cyclization to 6 and reaction with remaining aldehyde to 7 would competitively occur.

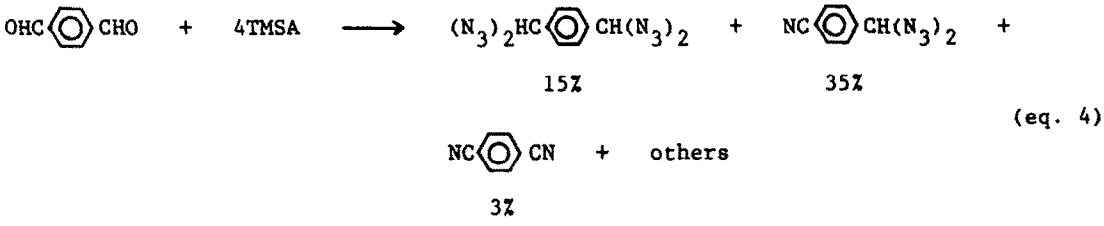
Formation of Nitriles[15)]

A variety of methods for preparing organic nitriles were established during the first half of this century.[16)] Among these methods, hydrazoic acid was known to convert aldehydes into nitriles. However, it is not easy to handle the acid and to control the quantity of this reagent. The reaction of aldehydes with excess hydrazoic acid often gives 5-amino-1*H*-tetrazoles. We tried to develop a direct (and a selective) procedure for the formation of nitriles from aldehydes using TMSA and $ZnCl_2$.

Treatment of benzaldehyde (1i), TMSA (2.3 equiv), and $ZnCl_2$ (1 equiv) gave benzonitrile (8i, 75%), *gem*-diazide 3i (trace), and 5-amino-1-phenyl-1*H*-tetrazole (2%). No 1-phenyl-1*H*-tetrazole (6i) was detected in the worked-up mixture. When the reaction of benzaldehyde and TMSA (2.3 equiv) in the presence of $ZnCl_2$ (0.06 equiv) in chloroform was carried out at the refluxed temperature for 20 h, a 42% yield of benzonitrile and a 24% of diazide 3i were isolated. Reactions of other aromatic and aliphatic aldehydes were also examined under various conditions and the results are shown in Table 3. With terephthalaldehyde, we obtained a mixture of products and characterized products are shown in equation 4.

Table 3. Formation of Nitriles (8) from Aldehydes and TMSA

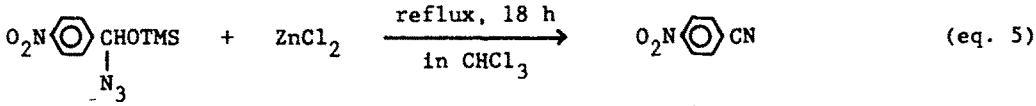
Aldehyde	Temp	Time/h	Products/% Nitrile 8	others
p-$MeOC_6H_4CHO$	r.t.	4	88	
p-MeC_6H_4CHO	r.t.	4	82	
C_6H_5CHO	r.t.	4	75	
p-ClC_6H_4CHO	r.t.	4	51	31 (36)
	r.t.	20	71	31 (13)
p-$O_2NC_6H_4CHO$	r.t.	4	trace	3m (88)
	reflux	20	53	6m (31)
m-$O_2NC_6H_4CHO$	r.t.	4	trace	3n (90)
	reflux	20	70	6n (19)
trans-cinnamaldehyde	r.t.	4	100	
2-furancarbaldehyde	r.t.	4	61	
2-thiophenecarbaldehyde	r.t.	4	trace	
	reflux	4	100	
n-BuCHO	reflux	20	5	6d (34)
n-$C_5H_{11}CHO$	r.t.	72	30	3h (4), 6h (63)
	reflux	20	27	6h (50)



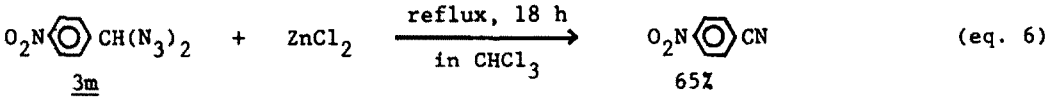
(eq. 4)

Aromatic aldehydes having electron-donating group and cinnamaldehyde gave the corresponding nitriles in high yields. A conversion of *m*- and *p*-nitrobenzaldehydes and 2-thiophenecarbaldehyde into nitriles could be achieved under relatively drastic conditions. The yields of aliphatic nitriles were not satisfactory and pyridinecarbaldehydes did not give nitriles at all under the employed conditions.

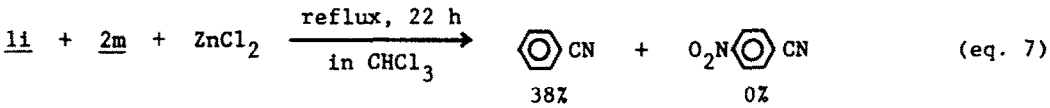
For the mechanistic study, decomposition of α-siloxy azide 2m and *gem*-diazide 3m was carried out. The former gave *p*-nitrobenzonitrile (8m) only in a 36% yield and the latter gave 8m in a 65% yield (eqs. 5 and 6). A mixture of benzaldehyde and 2m was found to give predominantly benzonitrile (eq. 7). These findings sug-



(eq. 5)



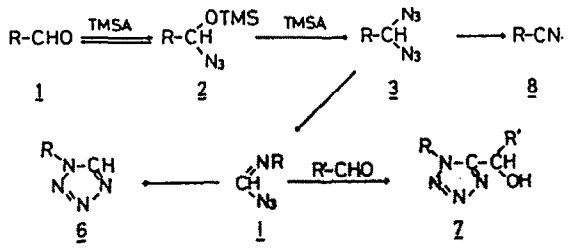
(eq. 6)



(eq. 7)

gest that diazide 3 but not siloxy azide 2 must be involved as an intermediate for the formation of nitrile and the addition process of TMSA to carbonyl group (step 1) should be reversible. During pyrolysis of aryldiazidomethanes having a hydroxyl group at *ortho* or *para* position of the benzene ring, similar nitrile formation was reported by Lindemann *et al.*[17]

In conclusion, the catalytic reaction of an aldehyde with TMSA takes place as in the Scheme. The conversion of an aldehyde into diazide, tetrazole, and nitrile could be selectively achieved by using TMSA (as one-pot reaction product), thus providing a simple and easy entry to this class of compounds.



Scheme

Experimental Section

Melting points are uncorrected. Infrared spectra were taken on a Hitachi 260-10 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were determined with a Hitachi R-600, Varian XL-100, or XL-300 spectrometer and a JEOL FX-60 spectrometer, respectively, using tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL DX-300 spectrometer.

Trimethylsilyl azide (TMSA), bp 95-96 °C, was prepared from chlorotrimethylsilane and sodium azide in butyl ether according to the literature.[7] Aldehydes were commercial products and purified if necessary.

Formation of Diazide

A) *gem*-Diazide (3)

A typical procedure is described for a reaction of benzaldehyde with TMSA. To a mixture of benzaldehyde (1i, 3.5 g, 33 mmol) and $SnCl_2 \cdot 2H_2O$ (0.45 g, 2 mmol) in 20 ml of anhydrous CH_2Cl_2 was added TMSA (9.5 g, 83 mmol) dropwise at 0 °C with stirring. And then the mixture was kept at room temperature for 20 h. The reaction mixture was poured into water and extracted with CH_2Cl_2. The dried extract was carefully evaporated *in vacuo* and the resulting residue was chromatographed on alumina. Elution with hexane gave 5.0 g (87%) of diazidophenylmethane (3i), of which purity was checked by spectroscopic analysis. MS, *m/z* 132 (M^+-N_3); IR (neat), ν_{max} 2100 cm^{-1} (N_3); ^{1}H NMR ($CDCl_3$), δ 5.60 (s, 1H) and 7.30 (s, 5H). The diazide was converted into 1-phenyl-1*H*-tetrazole, mp 65-66 °C (lit,[18] 65-66 °C), by the reported procedure.[6]

B) 1,3-Diazide (5)

To a solution of trimethylsilyl trifluoromethanesulfonate (955 mg, 4.3 mmol) in 14 ml of CH_2Cl_2 was slowly added dropwise a solution of 2-butenal (4a, 5.0 g, 71.3 mmol) and TMSA (20.5 g, 178 mmol) in 10 ml of CH_2Cl_2 at -78 °C. After addition was complete, the mixture was slowly warmed to room temperature and stirred for 20 h. Similar work-up to above gave a mixture of *E*- and *Z*-1,3-diazidobut-1-ene (6.0 g, 61%). An attempt of separation of the mixture failed. A treatment of 2-hexenal (4b) gave a mixture of *E*- and *Z*-1,3-diazidohex-1-ene in a 70% yield. The isomer ratio of the products was almost 3:2 in *E* and *Z*, determined by ^{1}H NMR spectra. 5a: IR (neat), ν_{max} 2100 cm^{-1} (N_3); MS, *m/z* 138 (M^+). 5b: IR (neat), ν_{max} 2100 cm^{-1} (N_3); MS, *m/z* 166 (M^+). ^{1}H NMR signals of 5a and 5b were assigned as follows by their coupling constans and intensities. ^{1}H NMR ($CDCl_3$), *E*-isomer of 5a: δ 1.32 (d, 3H, CH_3), 4.12 (m, 1H, H_c), 5.45 (dd, 1H, J_{ba}=14 Hz, J_{bc}=8 Hz, H_b), and 6.30 (d, 1H, J_{ab}=14 Hz, H_a). *Z*-isomer of 5a: δ 1.25 (d, 3H, CH_3), 4.60 (m, 1H, $H_{c'}$), 4.97 (dd, 1H, $J_{b'a'}$=7.5 Hz, $J_{b'c'}$=9 Hz, $H_{b'}$), and 6.50 (d, 1H, $J_{a'b'}$=7.5 Hz, $H_{a'}$). *E*-isomer of 5b: δ 0.91 (t, 3H, CH_3), 1.4 (m, $CH_2CH_2CH_3$), 3.95 (m, 1H, H_c), 5.35 (dd, 1H, J_{ba}=14 Hz, J_{bc}=9 Hz, H_b), and 6.25 (d, 1H, J_{ab}=14 Hz, H_a). *Z*-isomer of 5b: δ 0.94 (t, 3H, CH_3), 1.4 (m, $CH_2CH_2CH_3$), 4.75 (m, 1H, $H_{c'}$), 4.93 (dd, 1H, $J_{b'a'}$=7.5 Hz, $J_{b'c'}$=9 Hz, $H_{b'}$), 6.52 (d, 1H, $J_{a'b'}$=7.5 Hz, $H_{a'}$).

Formation of 1-Substituted Tetrazole (6)

As an example, a reaction of butanal (1b) with TMSA is representative. To a suspension of finely pulverized $ZnCl_2$ (7.2 g, 53 mmol) in 30 ml of anhydrous CH_2Cl_2 was added dropwise a solution of butanal (1b, 3.8 g, 53 mmol) and TMSA (18 g, 156 mmol) in 30 ml of CH_2Cl_2 at 0 °C with vigorous stirring. And then the mixture was allowed to stand at room temperature for 72 h with continuous stirring. The reaction mixture was poured into aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The dried CH_2Cl_2 extract was evaporated and chromatographed on silica gel. Elution with $CHCl_3$ afforded 4.6 g (78%) of 1-propyl-1*H*-tetrazole (6b). The ^{1}H NMR spectrum in $CDCl_3$ showed signals at δ 0.86 (t, 3H), 1.88 (m, 2H), 4.34 (t, 2H), and 8.58 (s, 1H). HRMS, calcd for $C_4H_8N_4$: *m/z* 112.0794, found *m/z* 112.0792 (M^+). The physical properties and spectral data of 1-substituted tetrazoles are shown in Table 4.

Table 4. 1-Substituted Tetrazoles

Compd	mp/°C	(lit)	^{1}H NMR/δ C_5-*H*	^{1}H NMR/δ others	MS, *m/z*	(calcd)
6a	liq		8.65	1.60 (t), 4.98 (q)	98.0571 (M^+)	(98.0592)
6b	liq		8.58	0.86 (t), 1.88 (m), 4.34 (t)	112.0742 (M^+)	(112.0749)
6c	liq		8.64	1.56 (d), 4.33 (m)	112.0745 (M^+)	(112.0749)
6d	liq		8.74	0.98 (t), 1.72 (m), 4.49 (t)	126.0913 (M^+)	(126.0905)
6f	liq		8.61	1.70 (s)	126.0941 (M^+)	(126.0905)
6h	liq		8.60	0.88 (t), 1.60 (m), 4.40 (t)	141.1177 (M^++*H*)	(141.1140)
6i	65-66	(65-66)[a]	9.18	7.62 (s)	147 (M^++1)	
6j	93-94	(93-94)[a]	9.02	2.40 (s), 7.36, 7.61 (ABq)	161 (M^++1)	
6k	116-117	(116-117)[a]	9.00	3.88 (s), 7.08, 7.65 (ABq)	176 (M^++1)	
6l	155-156	(155-156)[a]	9.05	7.65 (s)	181, 183 (M^++1)	
6m	201-203	(205)[b]	9.80	8.13, 8.42 (ABq)	192 (M^++1)	
6n	108-109		9.30	7.90-8.80 (m)	192 (M^++1)	
6q	179-180		9.20	8.04 (s)	171 (M^+)	

a) ref. 18. b) Freund, M; Paradies, T. *Chem. Ber.*, 1901, *34*, 3110.

Formation of 1,5-Disubstituted Tetrazole (7)

The following procedure is a representative of formation of 1,5-disubstituted tetrazoles. A solution of 2-methylpropanal (1c, 7.0 g, 97 mmol) and TMSA (13.4 g, 116 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a suspension of pulverized $ZnCl_2$ (13.2 g, 97 mmol) in CH_2Cl_2 (20 ml) at 0 °C with vigorous stirring. Work-up was similar to that described for tetrazole 6. Elution with $CHCl_3$ gave 4.0 g (45%) of 1-(1-methylethyl)-5-(1-hydroxy-2-methylpropyl)-1*H*-tetrazole (7c), colorless needles (hexane), mp 76-77 °C. In ^{1}H NMR spectrum which was determined at 300 MHz, 7c showed four doublets of methyl groups at δ 0.87 (J=6.7 Hz), 1.13 (J=6.7 Hz), 1.61 (J=6.8 Hz), and 1.62 (J=6.8 Hz), due to asymmetric carbon atom (C_α) attached to the tetrazole ring,[19] and others at δ 2.23, 4.73, and 4.94. ^{13}C NMR ($CDCl_3$), δ 18.42, 18.75, 22.73, 22.85, 33.72, 51.46, 70.57, and 154.90. Anal, Calcd for $C_8H_{16}N_4O$: C, 52.14; H, 8.76; N, 30.42%. Found: C, 52.02; H, 8.65; N, 30.64%. Table 5 lists the properties and the spectral data of compound 7. For compounds 7c and 7f, spin-spin coupling (J=*ca.* 7 Hz) between C_α-*H* and C_α-O*H* was observed in DMSO-d_6 and even in $CDCl_3$. By benzoylation of 7c, 5-(1-benzoyloxy-2-methylpropyl)-1-(1-methylethyl)-1*H*-tetrazole, mp 102-103 °C; IR (KBr), ν_{max} 1710 cm^{-1} (C=O); HRMS, calcd for $C_{15}H_{20}N_4O_2$: *m/z* 288.1586, found: *m/z* 288.1632, was obtained and the compound showed four doublets of the methyl signals for the two isopropyl groups at 0.95, 1.20, 1.61, and 1.69 ppm with J=*ca.* 6.5 Hz, even determined at 60 MHz.

Table 5. 1,5-Disubstituted Tetrazoles

Compd	mp/°C	^{1}H NMR/δ C_α-*H*	^{1}H NMR/δ others	MS, *m/z*	(calcd)
7a	38-39	5.00 (t)	0.99 (t), 1.95 (q), 1.52 (t), 4.54 (q)	156.1061 (M^+)	(156.1009)
7b	52-53	5.00 (m)	1.00 (t), 1.93 (m), 4.40 (q)	185.1423 (M^++*H*)	(185.1398)
7c	76-77	4.73 (dd)	0.87 (d), 1.13 (d), 2.23 (m), 1.62 (d) 4.94 (m)	185 (M^+)	
7f	124-125	4.83 (d)	1.01 (s), 1.78 (s)	213.1729 (M^++*H*)	(213.1710)

Formation of Nitrile (8)

A solution of TMSA (5.29 g, 46 mmol) in 15 ml of $CHCl_3$ was slowly added with stirring to a mixture of benzaldehyde (1i, 2.12 g, 20 mmol) and finely pulverized $ZnCl_2$ (2.72 g, 20 mmol) in 15 ml of $CHCl_3$ during 30-40 min at room temperature.

After stirred for 4 h, the mixture was poured into water and extracted with $CHCl_3$ (50 ml x 2). The dried extract over $MgSO_4$ was evaporated and the resulting residue was tritulated with hexane. The precipitated solid was filtered off and characterized to 5-amino-1-phenyl-1*H*-tetrazole [80 mg (2%), mp 157-158 °C (H_2O), lit,[20] 159.5-160 °C]. The filtrate was chromatographed on alumina, giving 1.54 g (75%) of benzonitrile (8i) with a trace of diazidophenylmethane (3i).

When *m*- and *p*-nitrobenzaldehydes were employed, *gem*-diazides 3n and 3m were obtained in 90 and 88% yields, respectively, under similar conditions. Therefore, a mixture of aldehyde, TMSA (2.3 equiv), and $ZnCl_2$ (1 equiv) in $CHCl_3$ (1.3 M) was refluxed for 4 h (for 2-thiophenecarbaldehyde) or 20 h (for nitrobenzaldehydes).

The results of these reactions are listed in Table 3 and all the product were identified by direct comparison with the authentic sample by at least two of the following methods: IR, NMR, MS, admixed melting points, and retenion time of VPC and HPLC.

A reaction of terephthalaldehyde was similarly carried out. A suspension of the aldehyde (1.34 g, 10 mmol), TMSA (5.29 g, 46 mmol), and $ZnCl_2$ (1.36 g, 10 mmol) in 15 ml of $CHCl_3$ was heated to reflux for 20 h. Similar work-up gave a mixture of products, including four identified products: α,α,α',α'-Tetraazido-*p*-xylene (3p, 390 mg, 15%), mp 56-58 °C; IR (KBr), 2100 cm^{-1}: MS, *m/z* 228 (M^+-N_3); ^1H NMR ($CDCl_3$), δ 5.70 (s, 2H) and 7.40 (s, 4H). *gem*-Diazido-*p*-cyanophenylmethane (3q, 700 mg, 35%), colorless liquid; IR (neat), 2230 (CN) and 2100 (N_3) cm^{-1}; MS, *m/z* 157 (M^+-N_3); ^1H NMR ($CDCl_3$), δ 5.80 (s, 1H) and 7.48, 7.69 (ABq, 4H). Terephthalonitrile (8q, 40 mg, 3%), mp 220-221 °C; IR (KBr), 2220 cm^{-1}; MS, *m/z* 128 (M^+). 1-(*p*-Cyanophenyl)-1*H*-tetrazole (6q, 150 mg, 9%), mp 179-180 °C; IR (KBr), 2210 cm^{-1}; MS, *m/z* 171 (M^+); ^1H NMR ($CDCl_3$), δ 8.04 (s, 4H) and 9.20 (s, 1H); Anal. Calcd for $C_8H_5N_5$: C, 56.13; H, 2.94; N, 40.92%. Found: C, 56.25; H, 2.94; N, 39.76%.

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