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The reaction of *N*-(4-dimethylaminophenyl)nitrones, **1**, with hydrogen azide proceeds via three distinct pathways to give a mixture of two tetrazoles, **5** and **9**, and a 2-azido-4-dimethylaminoaniline derivative, **6**. The proportions largely depend on the electron-withdrawing force resident in the function R attached to nitrone carbon. The formation of **5** constitutes a new synthetic approach to 1,5-disubstituted tetrazoles.

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Considering Kröhnke's note (1) that *N*-arylnitrones of type **1**, on treatment with cyanide and piperidine, yield α -cyano anils, **2**, and amidines, **3**, respectively, the simple sequence **1** \rightarrow **4** \rightarrow **5** might be envisaged as a novel route to 1,5-disubstituted tetrazoles (Scheme I, path 1). Earlier attempts in the author's laboratory (2) to verify this concept have disclosed that **1** (R = aryl) does indeed react with hydrogen azide (3), but the efforts remained unrewarded to the extent that they led to the "isomeric" benzylidene-*o*-azidoanilines **6** (path 2) (4) along with minor amounts of the nitriles **8** (path 3). However, traces of **5** could be detected in the case R = *p*-nitrophenyl.

This finding prompted a more detailed study on compounds **1** having electron-withdrawing groups R attached to nitrone carbon. It was assumed that electronegative moieties should facilitate proton abstraction from this position and thus favor tetrazole formation. Accordingly, the nitrones of two glyoxylamides (**1Ab,c**), of phenylglyoxal (**1Ad**), and of several isomeric tetrazole aldehydes (**1Ba-e**, **1Ca-c**) (**5**) were to be reacted and compared to the

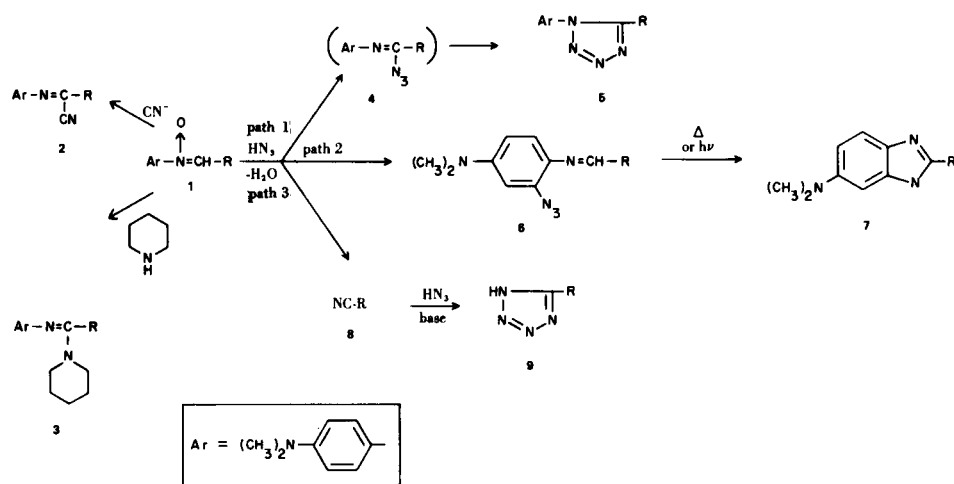
behavior of **1Aa**.

The preparation of **1Aa** (9), **1Ac** (10), **1Ad** (11), **1Ba-e** (6), and **1Ca** (12) has been described in the literature and achieved throughout by the Kröhnke reaction (1). Compound **1Ab** was obtained analogously from the known 1-(cyclohexylcarbamoylmethyl)pyridinium chloride (13). The nitrones **1Cb** and **1Cc** were made from the respective 5-chloromethyltetrazoles which were synthesized as follows: 5-Chloromethyl-2-(*p*-tolyl)tetrazole was prepared by lithium aluminum hydride reduction (14) of the corresponding carboxylic acid made after Dimroth and Merzbacher (15) or of its methyl ester and subsequent treatment of the resultant carbinol with thionyl chloride. The starting material for **1Cc** was provided by nitration of 5-chloromethyl-2-phenyltetrazole with fuming nitric acid (16).

Results.

When allowed to stand at room temperature, a solution of **1** and 3.5-4 equivalents of free hydrogen azide (ad-

Scheme I



A	R	B	R	R'	C	R	R'
a	<i>p</i> -NO ₂ C ₆ H ₄	a		C ₆ H ₅	a		C ₆ H ₅
b	CONHC ₆ H ₁₁	b		<i>p</i> -CH ₃ C ₆ H ₄	b		<i>p</i> -CH ₃ C ₆ H ₄
c	CONHC ₆ H ₅	c		<i>p</i> -NO ₂ C ₆ H ₄	c		<i>p</i> -NO ₂ C ₆ H ₄
d	COC ₆ H ₅	d	throughout	C ₆ H ₁₁		throughout	
		e	throughout	CH ₂ C ₆ H ₅			

Table I
Yields, Melting Points, and Analytical Data for **5**

5	Formula	Yield, %	M.p., °C	Calcd., % Found, %		
				C	H	N
Aa	C ₁₅ H ₁₄ N ₆ O ₂	5	202-205	58.06	4.55	27.08
				58.01	4.46	27.21
Ab	C ₁₆ H ₂₂ N ₆ O	10 (a)	146-148	61.13	7.05	26.73
				61.16	6.97	26.76
Ac	C ₁₆ H ₁₆ N ₆ O	22	154-156	62.33	5.23	27.26
				62.36	5.27	27.31
Ad	C ₁₆ H ₁₅ N ₅ O	50	116-117	65.52	5.15	23.88
				65.38	5.08	23.73
Ba	C ₁₆ H ₁₅ N ₉	33	202-203	57.65	4.54	37.82
				57.59	4.56	37.87
Bb	C ₁₇ H ₁₇ N ₉	61	174-175	58.78	4.93	36.29
				58.77	5.05	36.46
Bc	C ₁₆ H ₁₄ N ₁₀ O ₂	62	259-260 dec.	50.79	3.73	37.02
				50.74	4.03	37.23
Bd	C ₁₆ H ₂₁ N ₉	61	204-206	56.62	6.24	37.14
				56.20	6.42	37.31
Be	C ₁₇ H ₁₇ N ₉	36	169-171	58.78	4.93	36.29
				58.86	4.90	36.18
Ca	C ₁₆ H ₁₅ N ₉	8	168-170	57.65	4.54	37.82
				57.32	4.44	38.03
Cb	C ₁₇ H ₁₇ N ₉	8	185-186	58.78	4.93	36.29
				58.55	4.88	36.32
Cc	C ₁₆ H ₁₄ N ₁₀ O ₂	15	191-192 dec.	50.79	3.73	37.02
				50.83	3.76	37.13

(a) Besides 3% of *N*-cyclohexyl-*N'*-(4-dimethylaminophenyl)oxamide; m.p. 240° (recrystallized from ethanol); ms (*m/e*): 289, 162 (base peak), 136, 135. *Anal.* Calcd. for C₁₆H₂₃N₃O₂: C, 66.41; H, 8.01; N, 14.52. Found: C, 66.64; H, 7.76; N, 14.47.

Table II
Mass Spectral Data for **5**

Compound (Ion Source Temperature)	Molecular Ion <i>m/e</i> (% of Base Peak)	Base Peak	Other Important Fragments <i>m/e</i> (% of Base Peak)
Aa (320°)	310 (2)	282	283 (18), 281 (19), 252 (8), 237 (11), 236 (52), 235 (17), 192 (12), 145 (13), 134 (90), 133 (54), 119 (40)
Ab (170°)	314 (4)	161	162 (18), 160 (27)
Ac (210°)	308 (2)	161	280 (5), 162 (14), 160 (65), 146 (8), 145 (11), 144 (10), 134 (4), 133 (5), 120 (5), 119 (26)
Ad (220°)	293 (1)	105	265 (8), 160 (14), 144 (7)
Ba (150°)	333 (41)	134	334 (10), 277 (11), 276 (20), 262 (8), 234 (5), 185 (9), 161 (51), 160 (99), 159 (36), 145 (36), 144 (76), 135 (77), 133 (99), 119 (97), 118 (31), 117 (59)
Ca (150°)	333 (11)	134	334 (2), 305 (<1), 277 (3), 186 (26), 185 (13), 161 (7), 160 (56), 159 (5), 145 (11), 144 (11), 135 (20), 133 (41), 120 (12), 119 (27)

vantageously in methylene chloride/benzene as solvent) soon gave indications of appreciable reactivity. With **1Ad** the mixture had even to be cooled. Some days later, the rather facile work-up procedure afforded the desired tetrazoles **5** in all cases (Table I), but a careful product analysis revealed that again three competing reaction modes were operative. In addition to **5**, the 2-azido-4-dimethylaminoanils **6** and the *N*-unsubstituted tetrazoles **9** were found. While the yields of **9** were erratic (Table V) and individual figures can hardly be rationalized (save that of **9Aa**, see later), the proportions of **5** largely parallel the electron-attracting force of the ligand R on the nitrone carbon. Thus, the phenylglyoxalo nitrone **1Ad** gave higher yields of **5** than the glyoxylamido nitrones **1Ab** and **1Ac**. The same dependence became apparent with the isomeric nitrones **1B** and **1C**. Due to the stronger electron-withdrawing influence exerted by the 1-substituted 5-tetrazolyl system (17,18), the yields of the symmetric bi-tetrazoles **5B** were conceivably higher than those of the unsymmetric ones **5C**. All new tetrazoles of type **5** are stable, feebly basic compounds that can be extracted from mineral acid solution. Their structures are supported by analytical (Table I) and mass spectral data (Table II).

The yields of **6** also show some regularity, in particular with **6B** and **6C**. They were generally low in the **B** series, but reached 30% in the isomeric **C** series (e.g., **6Ca**). However, as these compounds in most cases could only be purified with considerable loss of material, exact yield figures have been omitted throughout. The presence of **6** was rather established from ir spectra, using a number of authentic samples (Table III), or simply demonstrated by hydrolysis to the 2-azido-4-dimethylaminoaniline which was in turn identified as picrate (2). Yet another, more specific characterization of **6** is at hand, viz. pyrolysis (19) to the benzimidazoles **7** (20), the formation of which occurs slowly even on standing in diffuse daylight (Table IV).

An important finding as to the proportions of **5** and **6** concerns the polarity of the solvent system used. For example, the routine reaction of **1Bb** gave a 60% yield of **5Bb** along with a negligible amount of **6Bb**; addition of solely 10 volume percent of ethanol produced a 1:1 mixture of about 25% yield each. Moreover, a reaction of **1Bb** in aqueous acetic acid afforded merely traces of **5Bb** but still 20% of **6Bb**.

The formation of the third major product, the *N*-un-

Table III

Melting Points, Ir (Potassium Bromide), and Analytical Data for **6** (Authentic Samples)

6	Formula	M.p., °C (dec.)	ν N ₃ , cm ⁻¹	Calcd., % Found, %		
				C	H	N
Ab	C ₁₆ H ₂₂ N ₆ O	135-136	2110	61.13	7.05	26.73
				61.06	6.91	26.50
Ba	C ₁₆ H ₁₅ N ₉	135-140	2110	57.65	4.54	37.82
				57.71	4.58	37.72
Bd	C ₁₆ H ₂₁ N ₉	169-170	2108	56.62	6.24	37.14
				56.53	6.24	37.21
Ca	C ₁₆ H ₁₅ N ₉	135-136	2110	57.65	4.54	37.82
				57.62	4.48	37.84

Table IV

Melting Points, Ir (Potassium Bromide), and Analytical Data for **7**

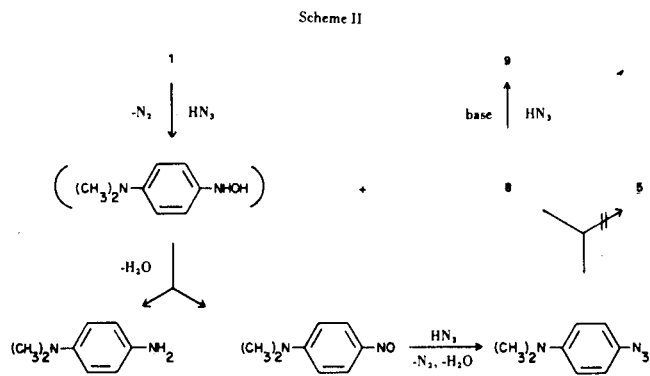
7	Formula	M.p., °C	ν NH, cm ⁻¹	Calcd., % Found, %		
				C	H	N
Ab	C ₁₆ H ₂₂ N ₄ O	251-255	3300 (a)	67.11	7.74	19.56
				67.16	7.69	19.74
Ba	C ₁₆ H ₁₅ N ₇	274-276	3230	62.94	4.95	32.11
				62.51	5.07	32.10
Bd	C ₁₆ H ₂₁ N ₇	291-294	3200	61.71	6.80	31.49
				61.68	6.81	31.35
Ca	C ₁₆ H ₁₅ N ₇	229-232 dec.	3290	62.94	4.95	32.11
				62.84	4.88	32.08

(a) Very broad absorption band.

Table V
Yields, Melting Points, and Analytical Data for 9

9	Formula	Yield, %	M.p., °C	Caled., % Found, %		
				C	H	N
Aa	C ₇ H ₅ N ₅ O ₂	trace (a)	218-219 (b)			
Ab	C ₈ H ₁₃ N ₅ O	25	228-229	49.22 48.74	6.71 6.59	35.87 35.72
Ac	C ₈ H ₇ N ₅ O	32	218-219 (c)			
Ad	C ₈ H ₆ N ₄ O	12	138-139 (d)			
Ba	C ₈ H ₆ N ₈	23	175-177	44.86 45.15	2.82 2.87	52.32 52.29
Bb	C ₉ H ₈ N ₈	19	202-204	47.37 47.60	3.53 3.53	49.10 49.24
Bc	C ₈ H ₅ N ₉ O ₂	4	193-195	37.07 37.07	1.94 1.88	48.64 48.44
Bd	C ₈ H ₁₂ N ₈	16	151-153	43.63 43.57	5.49 5.40	50.88 50.91
Be	C ₉ H ₈ N ₈	32	140-141	47.37 47.50	3.53 3.54	49.10 48.73
Ca	C ₈ H ₆ N ₈	37	217-219	44.86 44.89	2.82 2.89	52.32 52.58
Cb	C ₉ H ₈ N ₈ ·H ₂ O	30	215-217	43.90 44.04	4.09 3.83	45.51 45.16
Cc	C ₈ H ₅ N ₉ O ₂	31	199-202 dec.	37.07 37.13	1.94 1.87	48.64 48.48

(a) Besides 20% of **8Aa**. (b) Lit. m.p. (32) 219°. (c) Lit. m.p. (33) 220-221°. (d) Lit. m.p. (33) 140-141°.



substituted tetrazoles **9**, is tentatively summarized in Scheme II. The crucial step constitutes the fission of the C=N double bond in a pathway closely related to the Schmidt fragmentation of aldehydes. The resultant compounds undergo further reactions: The 4-dimethylaminophenylhydroxylamine is unstable with respect to disproportionation (21) to the corresponding aniline and nitrosobenzene, the latter being partly converted into 4-dimethylaminophenyl azide by excess hydrogen azide (22). The activated nitriles **8**, in the presence of weak base (23,24),

smoothly add 1 equivalent of the azide to produce **9** (save **8Aa** which is little affected). By contrast, another reaction mode of **8**, viz. the [2+3]-cycloaddition to the 4-dimethylaminophenyl azide to give **5**, can be ruled out as such a ring closure would require drastic conditions (25, 26).

The results obtained with the phenylglyoxalo nitrone **1Ad** deserve a separate comment. A C=N bond fission which proceeds quite rapidly in this instance gave rise to benzoyl cyanide, **8Ad**, which yielded a mixture of **9Ad** and benzoyl azide (27). Former attempts of other workers to add azide onto **8Ad** (28) have involved the formation of phenyl isocyanate since the experiments had been performed under inappropriate conditions. Free cyanide, produced above from **8Ad** and azide, then converted unreacted nitrone **1Ad** into Kröhnke's α -cyano anil **2Ad** (29). The main product itself, the 5-benzoyltetrazole **5Ad**, exhibits the expected behavior toward bases (30): On treatment with aqueous alkali or even partly when chromatographed on alumina, the benzoyl group is split off immediately to give the known 1-(4-dimethylaminophenyl)tetrazole (31). This provides an additional structure proof of **5**.

EXPERIMENTAL

General.

Melting points were determined on a Kofler microscope and are uncorrected. Spectral data were recorded as follows: Nmr was determined with a Varian T-60 (tetramethylsilane as internal standard throughout); ir was determined with a Leitz Unicam SP 200 G; ms by an AEI MS 9 (70 eV).

2-(*p*-Tolyl)-5-tetrazolecarboxylic Acid.

An aqueous solution (1+1) of glyoxylic acid (29.6 g., 0.2 mole) was dropwise added with stirring and ice-cooling to *p*-tolylhydrazine (24.4 g., 0.2 mole) in ethanol (100 ml.). The hydrazone began to separate at once. It was collected by filtration two hours later, washed with cold ethanol and light petroleum, and dissolved in 4% sodium bicarbonate solution; insolubles were filtered off. Addition of 6*N* hydrochloric acid to the filtrate precipitated yellow crystals (21.5 g., after drying over potassium hydroxide; m.p. 134°). Following the procedure described in reference (15), this material was directly reacted with 2,4,6-tribromophenyl azide (45 g.) in the presence of sodium ethoxide (3.14 g. of sodium, 100 ml. of absolute ethanol) to give a 24.0 g. yield (54%, based on *p*-tolylhydrazine); prisms (recrystallized from benzene), m.p. 179-180° dec.; ir (potassium bromide): ν C=O cm^{-1} , 1740.

Anal. Calcd. for $\text{C}_9\text{H}_8\text{N}_4\text{O}_2 \cdot \text{H}_2\text{O}$: C, 48.65; H, 4.54; N, 25.21. Found: C, 48.88; H, 4.10; N, 25.41.

Methyl 2-(*p*-Tolyl)-5-tetrazolecarboxylate.

The above acid was reacted with methanol and a trace of *p*-toluenesulfonic acid in the usual manner to give the ester in good yield; slightly colored needles, m.p. 109-111° (recrystallized from methanol); ir (potassium bromide): ν C=O cm^{-1} , 1745; nmr (deuteriochloroform): δ 2.44 (s, C-CH₃); 4.13 (s, O-CH₃); 7.30, 7.45, 7.98, 8.13 (AA'BB', H₄).

Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2$: C, 55.04; H, 4.62; N, 25.68. Found: C, 54.96; H, 4.47; N, 25.71.

5-Chloromethyl-2-(*p*-tolyl)tetrazole.

Lithium aluminum hydride (1.0 g.) was added portionwise to a stirred suspension of the above ester (8.72 g., 40 mmoles) in absolute ether (150 ml.). The reaction mixture was heated to reflux for four hours, then worked-up by addition of 2*N* sulfuric acid. The organic layer was separated and the aqueous phase repeatedly extracted with ether to give the crude carbinol (7.4 g.). Recrystallization from benzene yielded 5.88 g. of colorless prisms, m.p. 97-98°. The resultant filtrate was evaporated under reduced pressure and the oily residue again treated with lithium aluminum hydride to afford an additional 1.24 g. yield of the carbinol. The materials were combined, dissolved in chloroform (30 ml.) and refluxed with thionyl chloride (16 ml.) for two hours. On evaporation to dryness the product solidified. Recrystallization from ethanol gave a 6.86 g. yield (82%), coarse needles, m.p. 82-84°.

Anal. Calcd. for $\text{C}_9\text{H}_9\text{ClN}_4$: C, 51.81; H, 4.35; N, 26.85. Found: C, 51.67; H, 4.32; N, 26.82.

5-Chloromethyl-2-(4-nitrophenyl)tetrazole.

5-Chloromethyl-2-phenyltetrazole (7) (7.8 g., 40 mmoles) was stirred with fuming nitric acid (80 ml.) for two hours at 35°. Then the clear solution was poured over crushed ice and the product collected by filtration. Recrystallization from ethanol gave a 8.32 g. yield (87%), yellowish plates, m.p. 112-114°.

Anal. Calcd. for $\text{C}_8\text{H}_6\text{ClN}_5\text{O}_2$: C, 40.10; H, 2.52; N, 29.23. Found: C, 40.05; H, 2.39; N, 29.01.

N-Cyclohexylcarbamoylmethylene-4-dimethylaminazniline *N*-Oxide (1Ab).

A solution of 1-(cyclohexylcarbamoylmethyl)pyridinium chloride (13) (5.1 g., 20 mmoles) and *N,N*-dimethyl-*p*-nitrosoaniline (3.0 g., 20 mmoles) in ethanol (30 ml.) was cooled to 0°. Then 1*N* sodium hydroxide (20 ml.) was added with vigorous stirring. After one hour the suspension was diluted with water (100 ml.) and kept overnight in a refrigerator. The product was filtered off, washed with cold water, and air dried to give a crude yield of 4.7 g. (81%). Recrystallization from benzene afforded orange plates, m.p. 138-140°; nmr (deuteriochloroform): δ 7.53 (s, -N(O)=CH-).

Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{N}_3\text{O}_2$: C, 66.41; H, 8.01; N, 14.52. Found: C, 66.73; H, 8.34; N, 14.72.

From the benzene filtrate of 1Ab deposited some *N*-cyclohexyl-2-(4-dimethylaminophenylimino)acetamide; yellow needles, m.p. 173-174°; nmr (deuteriochloroform): δ 7.87 (s, -N=CH-).

Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{N}_3\text{O}$: C, 70.30; H, 8.48; N, 15.37. Found: C, 69.96; H, 8.64; N, 15.52.

N-[2-(*p*-Tolyl)-5-tetrazolylmethylene]-4-dimethylaminoaniline *N*-Oxide (1Cb).

A solution of 5-chloromethyl-2-(*p*-tolyl)tetrazole (4.17 g., 20 mmoles) and pyridine (3 ml.) in ethanol (5 ml.) was heated to reflux for two hours. On removing the solvent and excess pyridine under vacuum and adding THF, the pyridinium salt crystallized. The material was in turn reacted with *N,N*-dimethyl-*p*-nitrosoaniline as has been described in reference (6) to give a 5.5 g. yield (85%), yellow needles (recrystallized from benzene), m.p. 145-146°; nmr (deuteriochloroform): δ 8.43 (s, -N(O)=CH-).

Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_6\text{O}$: C, 63.34; H, 5.63; N, 26.07. Found: C, 63.50; H, 5.66; N, 26.53.

N-[2-(4-Nitrophenyl)-5-tetrazolylmethylene]-4-dimethylaminoaniline *N*-Oxide (1Cc).

This nitrone was obtained as above from 5-chloromethyl-2-(4-nitrophenyl)tetrazole (2.4 g., 10 mmoles) in a 3.18 g. yield (90%), red plates (recrystallized from benzene), m.p. 192-194° dec.

Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_7\text{O}_3$: C, 54.39; H, 4.28; N, 27.75. Found: C, 54.60; H, 4.23; N, 27.74.

Reaction of 1 with Hydrogen Azide (General Procedure).

The nitrone 1 (5 mmoles) was dissolved or suspended in pure methylene chloride (10 ml.). Then a solution of hydrogen azide in benzene (34) (7.5-8%, 12-13 ml.) was added, all at once, at room temperature (external cooling with 1Ad). Protected from light, the mixture gradually turned dark and turbid with slight evolution of gaseous nitrogen. After two or three days the solvent and excess hydrogen azide were removed under reduced pressure (35). The solid or oily residue was again dissolved in methylene chloride (50 ml.) (a) and washed with 4% sodium bicarbonate solution (4 x 5 ml.) (b).

(a) After the methylene chloride solution had been treated with bicarbonate, it was dried over sodium sulfate and concentrated. Except for 1Ad, the residual material was chromatographed on alumina using methylene chloride as eluent to give first substituted *N*-methylene-2-azido-4-dimethylaminoanilines, 6, and then 5-substituted 1-(4-dimethylaminophenyl)tetrazoles, 5 (reverse order in the B series). With 1Aa, a 20% yield of 8Aa was also obtained, identified by comparison (ir spectrum) with an authentic sample. In case of 1Ad, the resultant red oil was triturated with ethanol to give 5Ad along with 7% of 2Ad, identified by using an authentic sample (29); the presence of benzoyl azide was established by its

characteristic odor in connection with its absorption bands at cm^{-1} : 2140 and 1700 (comparison with an authentic sample). In Table I are presented yields, melting points, and analytical data for **5**; select mass spectral data are given in Table II. All compounds were recrystallized from ethanol except for **5Bc** (methanol).

(b) The combined bicarbonate washings were acidified with 12*N* hydrochloric acid to produce 5-substituted tetrazoles, **9**, which were isolated by filtration or repeated extraction with chloroform. Yields, melting points, and analytical data are listed in Table V. Recrystallization was effected by benzene (**9Ad**), ethanol (**9Cc**), ethanol/water (**9Ac**, **9Bb**, **9Bc**, **9Be**, **9Ca**, **9Cb**), ether/light petroleum (**9Bd**), and chloroform/light petroleum (**9Ab**, **9Ba**).

Reaction of **1Bb** with Sodium Azide in Acetic Acid.

Compound **1Bb** (1.61 g., 5 mmoles) was dissolved in glacial acetic acid (15 ml.) with gentle warming. Then sodium azide (1.46 g., 22.4 mmoles) in water (7.5 ml.) was added and the mixture held at ambient temperature for three days (protection from light). The work-up procedure given above afforded traces of **5Bb**, 0.2 g. (18%) of **9Bb**, and 0.35 g. (20%) of **6Bb**; orange needles (recrystallized from ethanol), m.p. 174° dec., ir (potassium bromide): $\nu \text{N}_3 \text{ cm}^{-1}$, 2110.

Anal. Calcd. for $\text{C}_{17}\text{H}_{17}\text{N}_9$: C, 58.78; H, 4.93; N, 36.29. Found: C, 58.86; H, 4.86; N, 35.91.

Substituted *N*-Methylene-2-azido-4-dimethylaminoanilines (**6**) (Authentic Samples).

A solution of equimolar amounts (3 mmoles) of 2-azido-4-dimethylaminoaniline (**2**) and *N*-cyclohexylglyoxylamide (**36**), 1-cyclohexyl-5-tetrazolecarbaldehyde (**6**), 1-phenyl-5-tetrazolecarbaldehyde (**6**), and 2-phenyl-5-tetrazolecarbaldehyde (**7**), respectively, in ethanol (10 ml.) was heated under reflux for ten minutes, after a few drops of glacial acetic acid had been added. On cooling, the product deposited in almost quantitative yield and was recrystallized from ethanol to give yellow or orange light-sensitive needles or plates. For melting points, ir, and analytical data see Table III.

2-Substituted 5(6)-Dimethylaminobenzimidazoles (**7**).

Compound **6** (2 mmoles) in *o*-dichlorobenzene (25 ml.) was heated with stirring for one hour to 140-150°. Compounds **7Ba**, **7Bd**, and **7Ca** precipitated on cooling to room temperature and were recrystallized from *o*-dichlorobenzene. The solution of **7Ab** was concentrated under vacuum and the solid residue recrystallized from ethanol/water. The yields were generally fair; melting points, ir, and analytical data are collected in Table IV. With the exception of **7Ca**, the compounds show strong fluorescence in uv light.

5-Cyano-1-cyclohexyltetrazole (**8Bd**).

A solution of 1-cyclohexyl-5-carbaldoxime (**6**) (7.8 g., 40 mmoles) in dry pyridine (50 ml.) and acetic anhydride (25 ml.) was heated to reflux for two hours. The mixture was then concentrated under vacuum and the residual solid recrystallized from ethanol/water to give a 6.7 g. yield (95%), prisms, m.p. 70-72°; ir (potassium bromide): $\nu \text{C}\equiv\text{N cm}^{-1}$, 2260.

Anal. Calcd. for $\text{C}_8\text{H}_{11}\text{N}_5$: C, 54.22; H, 6.26; N, 39.52. Found: C, 54.19; H, 6.37; N, 39.85.

This nitrile and 4-dimethylaminophenyl azide (**22**) (0.1 g. each) were kept in a 5% hydrogen azide solution (benzene/methylene chloride; 1 ml.) at room temperature for three days. After evaporation of the solvent, the dark residue was taken up in 4% sodium bicarbonate solution (5 ml.) and washed with methylene chloride. Addition of 12*N* hydrochloric acid and extraction with

chloroform afforded a crystalline material that proved fully identical to that obtained from **1Bd** (Table V, **9Bd**), m.p. 150-152°

Reaction of Benzoyl Cyanide, **8Ad**, with Hydrogen Azide.

Compound **8Ad** (1.6 g., 12 mmoles), hydrogen azide (10% solution in benzene, 25 ml.), and pyridine (1.3 ml.) in methylene chloride (25 ml.) were held at ambient temperature for two days. Following the work-up procedure described above, the mixture was concentrated, the residue treated with bicarbonate, washed with methylene chloride, and acidified to give a 1.15 g. yield (55%) of **9Ad**, plates (recrystallized from benzene), m.p. 138-140° (cf. Table V); ir (potassium bromide): $\nu \text{NH cm}^{-1}$, 2720 (very broad); $\nu \text{C=O}$, 1662.

The methylene chloride washings were dried and concentrated to afford a 0.8 g. yield (45%) of fairly pure benzoyl azide, identified by comparison (ir spectrum) with an authentic sample.

Reaction of **5Ad** with Sodium Hydroxide.

Compound **5Ad** (0.3 g., ca. 1 mmole) was suspended in ethanol (20 ml.). On addition of 2*N* sodium hydroxide the material dissolved immediately. After one-half hour the organic solvent was stripped and the residual mixture repeatedly extracted with methylene chloride to give a 0.18 g. yield (93%) of 1-(4-dimethylaminophenyl)tetrazole, light-sensitive plates (recrystallized from ethanol), m.p. 134-135°, lit. m.p. (31) 134-135°; nmr (deuteriochloroform): δ 3.06 (s, $-\text{N}(\text{CH}_3)_2$); 6.74, 6.90, 7.49, 7.63 (AA'BB', H_4); 9.00 (s, tetrazole ring); ms (m/e): 189, 161, 160, 145, 134 (base peak), 133, 119.

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