Thermal Decomposition of 1,4-Diaryl-1,4-dimethyl-2-tetrazenes[1]

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Abstract: First-order rate constants for decomposition of 1,4-dimethyl-1,4-diphenyl-2-tetrazene, its bis-*p*-methoxy, *p*-methyl, *p*-chloro, *p*-carbethoxy, and *m*-chloro derivatives, and the *p*-methyl-*p'*-carbethoxy derivative were determined in cumene at 110° and (for most) 125°. The unsymmetrical compound decomposes at a rate very close to the geometric mean of the two related symmetrical compounds. A Hammet σ–ρ plot fits σ^+ much better than σ, with a negative ρ. The decrease in rate with electron-withdrawing substituents is due to the $\Delta S^{\ddagger}$ term, not the $\Delta H^{\ddagger}$ term of the rate equation. Explanations of these observations are discussed.

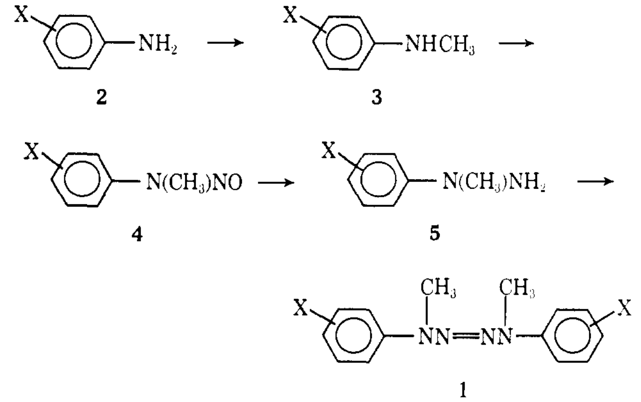
Reactive radicals with unpaired electrons on nitrogen have received much less study than the isoelectronic alkyl and alkoxy radicals. Wieland and Fressel reported the thermal decomposition of 2-tetrazenes to nitrogen and radical products in 1912,[3] and several 2-tetrazene decompositions have received study since. Five studies of 1,4-dimethyl-1,4-diphenyl-2-tetrazene decomposition (**1a**) have been published.[4]

Decomposition of a 2-tetrazene to nitrogen and amino radicals is expected to be analogous to azoalkane decomposition. Substitution of methyls and phenyl for hydrogens in azomethane causes remarkably regular changes in the activation parameters for thermal decomposition.[5]

For example, bis substitution of phenyl for methyl lowers $\Delta H^{\ddagger}$ by about 14 kcal/mol, and $\Delta S^{\ddagger}$ by some 6–7 eu. Tetramethyltetrazene has an E_a of 36.1 kcal/mol (vapor phase)[6] while **1a** is reported[4a] to give an E_a of 31.5 kcal/mol in cumene. Phenyl for methyl substitution in the 2-tetrazenes is much less effective at lowering the activation energy in 2-tetrazene than in azoalkane decomposition. We found it noteworthy that 2-tetrazenes are almost as stable as azoalkanes of comparable substitution, considering the rather large difference in dissociation energies for C–N bonds (75–80 kcal/mol) and N–N bonds (55–60 kcal/mol) in alkylamines and hydrazines.[7] To investigate the electronic factors involved in 2-tetrazene decompositions, we have prepared a series of 1,4-dimethyl-1,4-diaryl-2-tetrazenes and studied their decomposition rates.

Results and Discussion

Synthesis of the 2-tetrazenes was accomplished by standard methods. The anilines (**2**) were methylated to **3**, nitrosated to **4**, reduced to the hydrazine (**5**), and oxidized to the 2-tetrazene (**1**). With electron-withdrawing groups on the phenyl ring, extensive cleavage to the N-methylaniline was found to take place in the zinc reduction, but the presence of **3** does not affect the yield of the final step. N-Methyl-*p*-nitrophenylhydrazine (**5f**) was prepared by methylation of benzaldehyde *p*-nitrophenylhydrazone and hydrolysis.[8]



X =	X =
a, H	**e**, *p*-CO$_2$Et
b, *p*-OCH$_3$	**f**, *p*-NO$_2$
c, *p*-CH$_3$	**g**, *m*-Cl
d, *p*-Cl	**h**, *p*-CO$_2$Et, *p*-CH$_3$

Tetrazene decomposition was followed by nitrogen evolution in a constant volume apparatus with pressure transducer and strip-chart recorder.[9] The accuracy and reproducibility of kinetic data from our apparatus were determined by decomposing azoisobutyronitrile at 80.2° in cumene; five runs gave an average first-order rate constant of 1.59×10^{-4} sec^{-1} (maximum deviations $\pm\ 0.07 \times 10^{-4}$, less than 5%), in excellent agreement with the literature value[9] of 1.60×10^{-4} sec^{-1}. Rate constants for the tetrazenes studied, **1a–e**, **1g**, and **1h** at 110 and 125° in cumene, are summarized in Table I. The reproducibility of the kinetic data for the tetrazene decompositions was not particularly good, and maximum deviations of $\pm 7\%$ were found for the cases where several runs were made. At this level of accuracy the activation parameters which appear in Table I are clearly only qualitative. The activation energy for **1a**, calculated from the data of Erusalimsky and coworkers,[4d] is 31.5 kcal/mol, in reasonable agreement

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[2] Alfred P. Sloan Research Fellow.

[3] H. Wieland and H. Fressel, *Ann.*, **392**, 135 (1912).

[4] (a) A. Key and P. K. Dutt, *J. Chem. Soc.*, 2039 (1928); (b) R. G. Child, G. Morton, C. Pidacks, and A. Tomcutcik, *Nature*, 391 (1964); (c) McGowen and T. Powell, *Rec. Trav. Chim.*, **81**, 1061 (1962); (d) B. L. Erusalimsky, B. A. Dolgoplosk, and A. P. Kavunenko, *Zh. Obshch. Chim.*, 27, 267 (1957) (p 301 in the English translation); (e) K. M. Johnson, G. H. Williams, and H. J. Williams, *J. Chem. Soc.*, *B*, 1114 (1966).

[5] S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 137 (1966).

[6] B. G. Gowenlock, P. P. Jones, and D. R. Snelling, *Can. J. Chem.*, 41, 1911 (1963).

[7] B. G. Gowenlock, P. P. Jones, and J. R. Majer, *Trans. Faraday Soc.*, 57, 23 (1961).

[8] C. Rastetti and R. Ciusi, *Gazz. Chim. Ital.*, 52, 121 (1922).

[9] The apparatus was a simplified version of that of L. R. Mahoney, R. W. Beyma, A. Warnicle, and C. H. Rust, *Anal. Chem.*, 36, 2516 (1964).

Table I. Rate Constants[a] for Decomposition of Tetrazenes **1** in Cumene (Values Recorded are 10^4k (sec^{-1}))

Compd (X)	Temp, °C		$\Delta H^{\ddagger}$,[b]	$\Delta S^{\ddagger}$,[c]
	110.00	125.00	kcal/mol	eu
1b (*p*-OCH_3)	14.3 (5)	57.3[d]	33	15
1c (*p*-CH_3)	1.90 (5)	11.5 (3)	36	15
1d (*p*-Cl)	0.89 (2)			
1a (H)	0.60 (5)	3.26 (4)	34	10
1g (*m*-Cl)	0.25 (2)	1.13 (3)	30	−4
1e (*p*-CO_2Et)	0.07	0.33	31	−3
1g (*p*-CO_2Et, *p*-CH_3)	0.42 (2)	1.99 (2)	31	−1

[a] Maximum deviation of individual runs from the average recorded was ±7% in the cases where four or five runs were made. [b] Activation energies are probably not better than ±2 kcal/mol. [c] Probably at least ±4 eu. [d] Temperature at 120.00°. At 84.70°, $k = 7.3 \times 10^{-5}$.

with our data. Our reported rate constants for **1a** are somewhat smaller than those observed by these workers, which extrapolate to 0.69×10^{-4} sec^{-1} at 110° and 3.9×10^{-4} at 125° (15.0 and 15.3% larger than our numbers). Although they report only a 5% increase in observed rate constant in going from a 0.05 to 0.42 *M* initial **1a** concentration, we began to observe noticeable deviations from linearity in a first-order plot at 0.04 *M*, and all of our reported data is for initial tetrazene concentrations in the range 0.008–0.02 *M*. At higher concentrations we believe induced decomposition becomes increasingly important, even in cumene.

We made a series of attempts at using thiophenol as a scavenger, in hopes that the more stable thiophenoxy radicals would completely eliminate induced decomposition, even at higher concentrations. These were unsuccessful, since significant increases in rate constants were observed. For example, with **1c** at 0.05–0.13 *M* thiophenol concentration (four times the tetrazene concentration) the observed rate constant was 1.2 times that in the absence of thiophenol, although first-order kinetics were observed. No data from runs containing thiophenol were included in Table I.

The bis-*p*-nitro compound **1f** was too insoluble in cumene to be run; no nitrogen evolution was even detectable when the solid was heated at 125° in cumene. This compound was soluble in dimethyl sulfoxide, but at 125° the half-life was greater than 50 hr, making the decomposition too slow for study using our apparatus. For comparison, the unsubstituted tetrazene **1a** was run in DMSO, and the observed rate at 110° was 1.0×10^{-4}, only 1.7 times as fast as in cumene. Obviously the effect of solvent polarity on the decomposition rate is quite small, and bis-*p*-nitro substitution decreases the decomposition rate substantially.

The rate constant for decomposition of **1h**, the "mixed" tetrazene (*p*-CO_2ET, *p*-CH_3), is almost exactly that expected for equal influence of the two substituents on the decomposition rate, which would make $\Delta F^{\ddagger}(\mathbf{1h}) = 1/2[\Delta F^{\ddagger}(\mathbf{1c}) + \Delta F^{\ddagger}(\mathbf{1e})]$, and $k(\mathbf{1h}) = [(k(\mathbf{1c}) \times k(\mathbf{1e})]^{1/2}$. The calculated number is $0.36 \pm 0.03 \times 10^{-4}$, and observed $0.42 \pm 0.03 \times 10^{-4}$ at 110°, and $1.95 \pm 0.4 \times 10^{-4}$ *vs.* 2.3×10^{-4} at 125°. We take this as reasonable evidence for a symmetrical, two-bond cleavage.

Relative decomposition rates at 110° as well as the substituent constants used in Hammett correlations are collected in Table II.

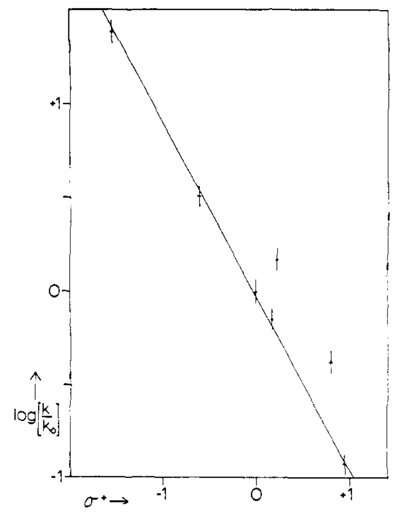


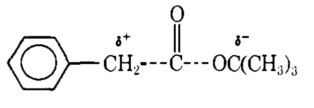
Figure 1. Hammett plot of **1** decomposition rates at 110° *vs.* σ^+.

The Hammett correlation with σ is poor, but a significant improvement is observed using σ^+ (Figure 1); five points are on a line ($\rho = 0.93$), but both the *m*- and *p*-chloro-substituted compounds give serious positive deviations. The halogens not filling Hammett correlations[10a] and unusually large *meta* effects[10b] have been previously noted for some radicals. The radical decomposition which gives a Hammett plot most similar to that of **1** is that of *t*-butyl arylperacetate (which follows σ^+, $\rho = -1.1$), studied by Bartlett and Rüchardt.[11] The interpretation is clearly that polar structures such as **6** make a significant contribution to the transition state.

Table II. Relative Decomposition Rates of Tetrazenes **1** at 110°

Compd (X)	k/k_H[a]	Substituent constants used for Hammett correlations		
		2σ	$2\sigma^+$	2σ(calcd)[b]
1c (*p*-OCH_3)	23.8 ± 3.5	−0.536	−1.56	−1.400
1b (*p*-CH_3)	3.2 ± 0.4	−0.340	−0.62	−0.510
1d (*p*-Cl)	1.48 ± 0.2	+0.454	+0.22	−0.116
1c (H)	1.00 ± 0.14	0	0	0
1g (*m*-Cl)	0.42 ± 0.06	+0.746	+0.798	
1e (*p*-CO_2Et)	0.12 ± 0.02	+0.900	+0.96	+0.842
1h (*p*-CH_3, *p*-CO_2Et)	0.70 ± 0.10	−0.280[c]	+0.17[c]	+0.166[c]

[a] Range is estimated with a 7% uncertainty in rate constants. [b] Calculated from data of Swain and Lupton. See text. [c] σ(*p*-CH_3) + σ(*p*-CO_2Et).



$$C_6H_5\overset{\delta+}{C}H_2{-}{-}{-}\overset{\overset{O}{\|}}{C}{-}{-}{-}\overset{\delta-}{O}C(CH_3)_3$$

6

For **1** decomposition, the combination of lack of a significant solvent effect with equality of substituent effects at each end of the tetrazene molecule rules out important contributions of such polar structures, and the reason for **1** decomposition following σ^+ must be different.

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(10) (a) R. I. Walters, *J. Am. Chem. Soc.*, **88**, 1923 (1966); (b) B. M. Latta and R. W. Taft, *ibid.*, **89**, 5172 (1967).

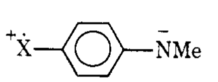
(11) P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1756 (1960).

An unusually great resonance effect is involved in the decomposition of **1**. To make $k_{p\text{-Cl}}/k_H$ 1.5 as observed, even a greater resonance contribution than that involved with σ^+ values is needed. Swain and Lupton[12] have proposed a method of breaking down substituent constants into field and resonance effects, using the relationship $\sigma = f\mathfrak{F} + r\mathfrak{R}$, where $\mathfrak{F}$ and $\mathfrak{R}$ are substituent constants, and f and r are characteristic of a reaction (different f and r values are required for *meta* and *para* substituents). An attractive feature of their treatment is that the relative amount of resonance ($\% R = 100 \cdot [r/(r + f)]$) is obtained, giving[12] σ_m as 22% R, σ_p 53%, and σ_p^+ 66%. Using this treatment, $f = 0.337$, $r = 1.678$ (83% R) puts *p*-Cl on a good line with the other *para* substituents, confirming the statement than an unusually large resonance contribution is involved.

From the limited data available, it is clear that the substituent effect upon **1** decompositions is substantially greater than that on similarly substituted azoalkanes. Bis-*p*-methoxy substitution on azo-1-phenylethane only increases the decomposition rate[13] by a factor of 1.31, and bis-*p*-methyl by 1.10.

Bis-2-tolyl-2-azopropane decomposes 1.46 times as fast as its phenyl analog.[14] The major factor influencing rate of azoalkane decompositions is radical stability. We shall first discuss the substituent effect which is expected for radical stability in the tetrazene decomposition.

Anilino radical should be less electrophilic than alkoxy radicals,[15] but still show inductive destabilization by electron-withdrawing groups (negative ρ). Resonance stabilization should be more effective than in carbon radicals, since odd electron delocalization gives contributing structures such as **7**, with a nitrogen to receive the negative charge. Unusually large *meta* substituent resonance contributions are also predicted, due to the possibility of direct resonance interaction as shown in **8**. With $-R$ groups resonance delocalization and inductive effect are opposed. The general problem substituent effects on radical stability has recently been discussed by Walters,[10a] who concluded it was not possible to predict whether $-R$ groups would stabilize or destabilize anilino radicals, but preferred the former. The argument used was that odd electron delocalization must compete with line pair delocalization, which becomes more favorable with better electron-withdrawing substituents. In the extreme, lone pair delocalization would force the odd electron into an sp^2 orbital on nitrogen. Since it is difficult to know where to place the energy of an sp^2 orbital on nitrogen in relation to the MO's of the π system, a definite prediction is difficult to make.



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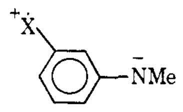

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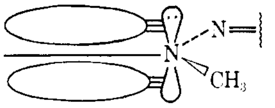
Although the trend of our rate constants for **1** decomposition is reasonable for radical stability, we do not believe that radical stability is very important in determining the rate. Our activation parameters are obviously qualitative (Table I), but there is certainly no evidence for $\Delta H^{\ddagger}$ increasing as the substituent is changed from *p*-methoxy to *p*-carbethoxy—if anything, there is a decrease. Instead, all of the rate decrease is caused by the $\Delta S^{\ddagger}$ term. The tetrazenes are in conformation **9**, with the lone pair essentially in a p orbital which overlaps with the aromatic π system. But for maximum stabilization of the anilino radicals forming in the decomposition, conformation **10** (nitrogen–nitrogen bond which is breaking perpendicular to the aromatic ring, lone pair in an unconjugated sp^2 (N) orbital) is required. We believe the substituent effect observed reflects the ease of obtaining conformation **10**, which is more difficult with *p*-carbethoxy than *p*-methoxy substituent, since the conjugation energy of the lone pair must be overcome.



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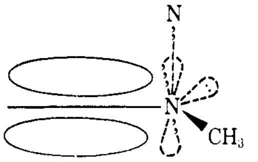

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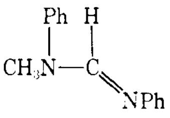
Our data do not indicate that N-methylanilino radicals with electron-withdrawing substituents are appreciably less stable than those with electron-releasing substituents (which, if true, ought to be reflected in an increasing $\Delta H^{\ddagger}$ term), but that an increasingly unfavorable conformation must be attained in order to delocalize the forming radical. The assumption[10a] that lone pair delocalization will always "win" over single electron delocalization may well not be justified. Since the effect of substituent on the stability of the radical formed and on the ease of attaining the proper conformation should be in the same direction, however, the relative importance of the two is difficult to access.

The material balance in our product studies of **1a** decomposition was never very good, and large amounts of intractable tars were obtained. At initial tetrazene concentrations of 0.1 *M*, a plethora of products was obtained, including a few per cent of N-methyl-N,N′-diphenylformamidine (**11**). Reducing the concentration of tetrazene to 0.008 *M* entirely eliminated the formation of **11**, suggesting that it is a product of induced decomposition. One obvious product which must be formed by disproportionation of N-methylanilino radicals is N-phenylformaldimine (**11**), which is well known to trimerize to **12**. No **12** was ever detected among our products, suggesting that **11** scavanges radicals more rapidly than it trimerizes, probably giving some of



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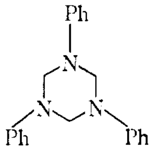

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$Ph(CH_3)_2CN(CH_3)Ph$
13

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[12] C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, **90**, 4328 (1968).

[13] S. G. Cohen, S. J. Groszos, and O. B. Sparrow, *ibid.*, **72**, 394 (1950).

[14] J. R. Shelton, C. K. Liang, and P. Kovacic, *ibid.*, **90**, 354 (1968).

[15] (a) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957; (b) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, Chapter 12.

the intractable material observed (although this would be an obvious source of **11**). Substantial amounts of N-methyl-N-cumylaniline (**13**), the "cross-coupling" product with cumyl radicals, were found, but control experiments showed that it was thermally unstable under our reaction conditions. How much was lost this way is unknown, for we were unable to make this amine by several routes, and never had enough to study carefully. In contrast to a recent report,[2e] N,N′-dimethylhydrazobenzene is formed, although in small amounts. It proved to be stable for 1 week at 110°, but does decompose at higher temperatures. Nitrogen yields were close to quantitative. Results are summarized in Table III. From Table III it is apparent that all of the N-methylaniline formed was not isolated, because 43.8, 47.3% of products containing cumyl radicals were found (compared to 31.0, 31.5% of N-methylaniline), and each cumyl radical must logically arise from abstraction of N-methyl-N-phenylamino radical. Additional N-methylaniline should also have arisen from disproportionation of N-methylanilino radicals. The reason for loss of N-methylaniline is still not apparent.

Table III. Products from the Thermal Decomposition of **1a** (Two Runs) in Cumene at 110° (7 Days, 0.008 *M* Initial Concentration)

	Pressure, mm	Yield, %
Starting tetrazene **1a**	2.87, 2.87	
Dicumyl	0.95, 1.12	33.2, 39.0
N-Methylaniline	1.78,[a] 1.81[b]	31.0, 31.5
N,N′-Dimethylhydrazobenzene	0.174, 0.194	6.1, 6.8
N-Cumyl-N-methylaniline (**13**)	0.608, 0.475	10.6, 8.3

[a] Isolated by tlc. [b] Distillate analyzed by vpc (naphthalene standard).

In conclusion, we interpret the much greater substituent effect on the decomposition rate of **1** compared to similarly substituted azoalkanes to be largely caused by differences in the ease of attaining the proper conformation for decomposition (nitrogen leaving perpendicular to the plane of the aryl groups). Since the substituent effect on radical stability ought to be in the same direction, however, it is difficult to access the relative importance of the two effects from rate studies alone. What is clearly needed is an independent measure of odd electron delocalization in N-aryl-N-alkylamino radicals, such as could be provided by esr, and experiments to provide such data are under way.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. Combustion analyses were by Spang Microanalytical Laboratories and were performed on material used for kinetic runs. Ir spectra were recorded on a Beckman IR-8, nmr spectra on a Varian A-60 or A-60A and are given in parts per million downfield from internal TMS, and uv spectra were recorded on Cary 11 or 15 instruments. Cumene was purified by shaking with concentrated sulfuric acid followed by distillation from sodium[16] through a 40-cm glass helices packed column.

1,4-Dimethyl-1,4-diphenyl-2-tetrazene (1a) was prepared by the procedure of Nathan and Goldschmidt.[17] Two recrystallizations from carbon tetrachloride gave a 50% yield of **1a** (based on 1-methyl-1-phenylhydrazine), mp 141–142° dec (lit.[18] mp 141°).

Anal. Calcd for $C_{14}H_{16}N_4$: C, 69.97; H, 6.71; N, 23.32. Found: C, 70.09; H, 6.72; N, 23.25.

Nmr analysis showed ($CDCl_3$) δ 3.62 (5.3), 7.25 (m, 4); uv (max) ($CHCl_3$) 347 nm (ϵ 2.8×10^4), 310 sh (1.2×10^4), 247 (8.4×10^3); (1,2-dimethoxyethane) 347 (3.1×10^4), 305 sh (1.3×10^4), 251 (1.5×10^4).

N-Methyl-N-nitroso-*p*-toluidine (4c) was prepared by a literature method,[19] by cooling a mixture of 98 g (0.807 mol) of N-methyl-*p*-toluidine,[20] 117 ml of concentrated HCl, and 325 g of crushed ice in an ice bath while 56.6 g (0.807 mol) of sodium nitrite in 200 ml of water was added over 30 min, keeping the temperature below 30°. After 1 hr the mixture was extracted four times with ether, the ether layer dried and concentrated, and the residue distilled, giving 46 g (38%) of nitroso compound, bp 105–111° (0.2 mm); after one crystallization from ethanol: mp 48–49° (lit.[21] mp 52–53°); nmr (CCl_4) δ 2.35 (s, 3), 3.30 (s, 3), 7.0–7.5 (m, 4).

N-Methyl-N-*p*-tolylhydrazine (5c) was prepared by a modification of the method of Hartman and Roll.[22] A mixture of 84 g of zinc dust and 125 ml of water was stirred a 10–20° while 46 g of **4c** in 140 ml of acetic acid was added dropwise. After stirring 2 hr and heating to 80°, the mixture was filtered and washed with three 100-ml portions of 5% hydrochloric acid, and the aqueous filtrate basified with 1.5 l. of 20% sodium hydroxide and extracted with five 100-ml portions of ether. After drying and concentrating, the hydrazine was distilled, giving 33.2 g (93%), bp 84–85° (1.0 mm).

1,4-Dimethyl-1,4-bis-*p*-tolyl-2-tetrazine (1c) was prepared using the lead dioxide oxidation of Nathan and Goldschmidt. From 5.0 g of hydrazine **5c**, 1.46 g (29.8%) of the tetrazene was obtained after two crystallizations, mp 148–149° dec.

Anal. Calcd for $C_{16}H_{20}N_4$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.81; H, 7.37; N, 20.85.

Uv (max) analyses showed ($CHCl_3$) 350 nm (ϵ 2.9×10^4), 317 sh (1.7×10^4), 248 (1.1×10^4); (1,2-dimethoxyethane) 348 (3.1×10^4), 315 sh (1.6×10^4), 253 (1.7×10^4).

N-Methyl-N-nitroso-*p*-anisidine (4b) was prepared from *p*-anisidine by the method of Klaus and Baudish[23] in 20% yield: mp 48–49° (lit.[24] mp 51°); nmr ($CDCl_3$) δ 3.38 (s, 3), 3.81 (s. 3), 7.14 (q, 4).

1,4-Dimethyl-1,4-bis(*p*-anisyl)-2-tetrazene (1b). To 2.0 g (0.013 mol) of N-methyl-N-*p*-anisylhydrazine (**5b**) (prepared[20] in 50% yield from the N-nitroso compound, 93–103° (7 mm)) stirring at −10° in 150 ml absolute ethanol was added 1.57 g of sublimed quinone in 60 ml of absolute ethanol, and the mixture was stirred 30 min and filtered. After two recrystallizations from chloroform, 0.53 g (26%) of tetrazene, **1b**, mp 152° dec, was obtained. Oxidation with lead dioxide, mercuric oxide, and potassium bromate all failed, largely cleaving the hydrazine.

Anal. Calcd for $C_{16}H_{20}N_4O_2$: C, 63.98; H, 6.71; N, 18.65. Found: C, 64.08; H, 6.78; N, 18.70.

Uv (max) analyses showed ($CHCl_3$) 352 nm, 323 sh, 245, but rapidly turns purple; (1,2-dimethoxyethane) 350 (2.9×10^4), 319 sh (2.1×10^4), 247 (1.1×10^4).

N-Methyl-N-nitroso-*p*-chloroaniline (4d). From 80 g (0.608 mol) of *p*-chloro-N-methylaniline (bp 78° (1.7 mm), prepared in 50% yield[20]) was obtained[19] 25.5 g (24%) of orange nitroso compound: mp 48–50° (ethanol–water); nmr (CCl_4) δ 3.33 (s, 3), 7.42 (m, 4).

N-Methyl-4-chlorophenylhydrazine (5d) was prepared by zinc reduction, as for **3d**, but 88.6 g of nitroso compound only gave 20.3 g (24%) of hydrazine: bp 89–93° (0.6 mm); nmr (CCl_4) δ 2.62 (s, 3), 3.55 (s, 2), 7.6 (m, 4). The low yield was caused by extensive cleavage to the aniline, which probably contaminated our product.

1,4-Dimethyl-1,4-bis(4-chlorophenyl)-2-tetrazene (1d) was prepared by lead dioxide oxidation in benzene at room temperature for 10.5 hr, giving 41% crude product. Several recrystallizations from carbon tetrachloride gave white needles, mp 169° dec.

Anal. Calcd for $C_{14}H_{14}N_4Cl_2$: C, 54.39; H, 4.56; N, 18.12; Cl, 22.93. Found: C, 54.34; H, 4.61; N, 18.17; Cl, 22.94.

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Uv (max) analyses showed ($CHCl_3$) 357 nm (ϵ 3.3 $\times$ 10^4), 318 sh (1.7 $\times$ 10^4), 252 (8.1 $\times$ 10^3); (1,2-dimethoxyethane) 354 (3.1 $\times$ 10^3), 315 sh (1.6 $\times$ 10^4), 254 (1.7 $\times$ 10^4).

Ethyl N-nitroso-4-aminobenzoate (4e) was prepared[23] in 47% yield from the aniline: mp 55–56° (ethanol-water); nmr (CCl_4) δ 1.38 (t, 3), 3.38 (s, 3), 4.35 (q, 2), 7.82 (q, 4).

1,4-Dimethyl-1,4-bis(4-carbethoxyphenyl)-2-tetrazene (1e) was prepared by lead dioxide oxidation of the hydrazine (71% yield by zinc dust reduction of the nitroso compound), mp 58–60° (alcohol), in 63% yield. Several extractions of the lead dioxide with boiling methylene chloride were required to separate this insoluble tetrazene, mp 180–181° dec.

Anal. Calcd for $C_{20}H_{24}N_4O_4$: C, 62.49, H, 6.29; N, 14.57. Found: C, 62.54; H, 6.24; N, 14.68.

Uv (max) analyses showed (1,2-dimethoxyethane) 3.77 nm (4.5 $\times$ 10^4), 297 (6.4 $\times$ 10^3), 268 (7.8 $\times$ 10^3), 230 (1.6 $\times$ 10^4).

N-Methyl-4′-nitrophenylhydrazine was prepared[3] by steam distilling 20 g of the N-methylbenzaldehyde 4-nitrophenylhydrazone (mp 134.0–134.5°) in 200 ml of concentrated hydrochloric acid for 10 hr. The mixture was filtered and saturated with sodium acetate, and yellow needles of a mixture of the hydrazine and the aniline precipitated upon cooling. The hydrazine was fractionally crystallized: mp 155–156° (lit.[25] mp 159°); nmr ($CDCl_3$) 3.29 (s, 3), 3.90 (broad s, 2), 4.68 (broad s, 1), 6.25–8.1 (m, 4).

1,4-Dimethyl-1,4-bis(4-nitrophenyl)-2-tetrazene (1f) was prepared by stirring the mixture of hydrazine and amine (*ca.* 1:1) obtained above (2.18 g), 16.8 g of lead dioxide, and 16.8 g of sodium sulfate in 100 ml of 1,2-dimethoxyethane for 4 days, and soxhlet extraction of the residue with acetone. After crystallization from dimethyl sulfoxide, 0.245 g (15%), mp 231° dec, was obtained (lit.[4b] mp 238°; our material is not photostable, as these authors claim).

Anal. Calcd for $C_{14}H_{14}N_6O_4$: C, 50.91; H, 4.17; N, 25.43; O, 19.39. Found: C, 51.02; H, 4.16; N, 25.39.

Uv (max) analyses showed ($CHCl_3$) 435 nm (ϵ 5.4 $\times$ 10^4), 293 (5.5 $\times$ 10^3), 263 (9.7 $\times$ 10^3).

1,4-Dimethyl-1,4-bis(3-chlorophenyl)-2-tetrazene (1g) was prepared by lead dioxide oxidation of the 1:3 amine–hydrazine mixture, bp 88–89° (0.8 mm), resulting from reduction of the N-nitroso compound, bp 80° (0.25 mm), with zinc. The tetrazene melts at 125–127° dec.

Anal. Calcd for $C_{14}H_{14}N_2Cl_2$: C, 54.39; H, 4.56; N, 18.12; Cl, 22.93. Found: C, 54.34; H, 4.75; N, 18.15, Cl, 23.06.

Uv (max) analyses showed (1,2-dimethoxyethane) 352 nm (ϵ 4.0 $\times$ 10^4), 310 (sh, 1.7 $\times$ 10^4), 248 (1.3 $\times$ 10^4).

1,4-Dimethyl-1-(4′-tolyl)-4-(*p*-carbethoxyphenyl)-2-tetrazene (1h). A mixture of 0.155 mol of each hydrazine, 40 g of lead dioxide, and 40 g of sodium sulfate was stirred 21 hr, filtered, and concentrated. The residue was chromatographed on 200 g of silica gel and eluted with benzene, yielding 0.39 g of **1c**, 0.80 g of **1e**, and 1.40 g of **1h**. Two crystallizations from 95% ethanol gave 1.10 g (34%): mp 118–119° dec; nmr (acetone-d_6) δ 1.33 (t, 3), 2.28 (s, 3), 3.50 (s, 3), 4.30 (q, 2), 7.20 (m, 4), 7.63 (m, 4); uv (max) 1,2-dimethoxyethane) 367 nm (ϵ 4.3 $\times$ 10^4), 305 (sh, 7.9 $\times$ 10^3).

N-Phenylformaldimine trimer was prepared by the method of Tollens:[26] mp 143–145°; ir indistinguishable from that published;[27] nmr ($CDCl_3$) δ 4.80 (s, 2 H), 6.6–7.5 (m, 5 H).

N,N′-Dimethylhydrazobenzene was prepared by the method of Reesor and Wright:[28] mp (repeated crystallization from methanol) 33–34° (lit.[27] mp 32.5–33°); nmr (CCl_4) δ 2.94 (s, 6), 6.58–7.20 (m, 10).

N-Methyl-N,N′-diphenylformamidine was prepared from aniline and N-methylformanilide by the method of Mandel and Hill[29] giving 30%: bp 136–138° (0.2 mm); ir 6.20, 6.37, 6.76 μ, identical with material isolated by vpc from the thermal decomposition of **1a** in cumene (0.1 *M*).

Kinetics. The kinetic apparatus consisted of a Dynisco PT-85 pressure transducer connected by a stainless steel joint to a bulb with side arm and stopcock with a joint for evacuation. Apiezon T grease was best to prevent leaks from developing. The reaction vessel was kept isothermal to ±0.02° with a 10-gallon oil bath and a 75-W light bulb controlled by a "magnaset" thermoregulator and electronic relay for fine heating control. The reaction mixture was stirred magnetically by use of a flexible shaft. A B.F. Model 1-1105 transducer input conditioner was used to apply voltage across the arms of the strain gauge, and the output signal was recorded on a Varian G-10 or Heath recorder. First-order rate constants were calculated from least-squares lines through kinetic points recorded over 2–4 half-lives; usually about 100 points were used. Blank runs showed 3–5 min were required for temperature equilibration after immersion into the bath; 7–15 min were used in all cases except **1b**, where 4.5-min equilibration was allowed before reading of kinetic points.

Product Study of 1a Decomposition. A mixture of 0.700 g of **1a** and 360 ml of cumene was heated and stirred under nitrogen for 7 days. Cumene was then distilled from the mixture at 43° (9 mm). Vpc analysis showed only the presence of cumene. The residue was eluted with pentane from a silica gel PF·254 tlc plate, separating the dicumyl. The other products were eluted three times with benzene; the N-methylaniline streaked badly, and may well be too volatile to be determined quantitatively this way. Vpc analysis of a separate run in which the N-methylaniline was distilled from the other products gave a similar yield, however.

N-Methyl-N-cumylaniline (13) was obtained only as a mixture with N-methylaniline from the tlc plates, and we were neither able to crystallize nor synthesize it. The nmr showed singlets at δ 1.42 (6 H), 2.62 (3 H), and a multiplet at 6.68–7.65 (10 H). Vapor phase chromatography on a 20% DC 710 column at 168° column temperature completely decomposed **13** to only N-methylaniline and α-methylstyrene, presumably by acid-catalyzed decomposition in the injection port. A sample heated 5 days at 110° in cumene underwent partial decomposition, but these products were not determined.

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