N-tert-Butylanilino Radicals

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Abstract: The rate-inhibiting effect of a *p*-carboethoxy substituent on nitrogen evolution from 1,4-diaryl-1,4-dimethyl-2-tetrazene is completely eliminated by introduction of an *o*-methyl substituent, ruling out radical stability as being the major factor controlling decomposition rate, and substantiating the previous claim of a conformational change being required prior to bond cleavage. The synthesis of seven 1,4-diaryl-1,4-di-*tert*-butyl-2-tetrazenes is reported, and the esr splittings of six *N-tert*-butylanilino radicals are presented. The nitrogen splitting is highest in the unsubstituted radical, placing these radicals in Walter's "class S." The $Q(N)$ values for amino radicals fall in the order $Ar_2N\cdot > ArRN\cdot > R_2N\cdot$.

The effect of substituents upon odd-electron delocalization in benzylic-type ($ArX\cdot$) radicals has been the subject of considerable discussion[1] since the discovery that triarylmethyl radical dissociation constants did not follow a Hammett correlation. Walter[2] has given the most complete discussion of the structural features controlling the sort of substituent effects observed, dividing radicals into "class O" (opposite direction of effect for electron donation and releasing substituents) and "class S" (same direction of effect) using such criteria as esr and uv spectra and stability. Class O radicals, which follow Hammett behavior,[3] all have two or more resonance forms which allow either a lone pair or an odd electron to be placed on the benzylic atom. Lone pair is preferable to odd-electron delocalization with electron-accepting substituents, whereas only odd-electron delocalization is possible with electron-donating substituents, leading to class O spectral trends. Examples include $Ar_2NO\cdot$, $ArNO_2\cdot^-$, $Ar_2CO\cdot^-$, and $Ar_2N\dot{N}(CO)R$. Class S radicals were suggested to be those in which only an odd electron was available for delocalization, including $Ar_3C\cdot$, $Ar_3N\cdot^+$, $Ar_3B\cdot^-$, and $Ar_2NNAr_2\cdot^+$. Here one would expect to delocalize the odd electron to both types of substituents and observe non-Hammett behavior. There has actually been little evidence for class S radicals. The dissociation data on triarylmethyl radicals undoubtedly need reinvestigation,[1,3] and the ortho splittings of triarylphenyl radicals show, if anything, a slight class O trend.[3,4] Although Walter[2] did report class S substituent effects for the esr splittings of triarylaminium ions (in formic acid), Latta and Taft[5] observed class O behavior for five such compounds (in acetonitrile), as well as for *N,N*-dimethylaminium ions (although there was a lot of scatter for meta substituents in a Hammett plot). In his review,[3] Janzen concluded that there were not enough data to justify Walter's class S on the basis of esr data.

Branch and Calvin[6] originally used diarylamino radicals as their prime example of what Walter calls a class O radical. Walter, however, is rather noncommittal on the type of substituent effects which should be observed, placing arylamino and diarylamino radicals in a special "possibly class O" category. Here both a lone pair and an odd electron are present on the benzylic atom at the same time, and delocalization of the two is placed in direct competition; lone-pair delocalization would require odd-electron localization on an sp^2 orbital, or rehybridization. Walter even suggests that the type of substituent effect observed might depend on the property studied.

A certain amount of experimental evidence seems to point to class O behavior for diarylamino radicals. Wieland's group reported[7] a class O stability order for tetraarylhydrazine decomposition to the radicals, with the 4-nitro-substituted compound being the most stable. Neugebauer and Fischer[8] did esr studies and were unable even to detect diarylamino radicals unless electron-releasing substituents were present, although Neugebauer and Bamberger[9] were later able to build up high enough concentrations of diphenylamino radical for esr studies by photolysis of the hydrazine in a flow system.

We had originally hoped to study the stability of arylamino radicals by measuring the decomposition rates of substituted 1,4-diaryl-1,4-dimethyl-2-tetrazenes (**1**), using the analogy to the excellent correlation of azo compound decomposition rates with the stability of the carbon radical formed. Although we did observe[10] a fairly large decrease in rate which gave a reasonable Hammett correlation as the aryl substituent was changed from 4-methoxy to 4-carboethoxy (rate ratio of about 200 at 110°, ρ about 0.93), our final conclusion was that these rates did not reflect radical stability or amount of delocalization. This was based upon an admittedly crude activation parameter study, which showed that the entire rate decrease in going from **1**($4\text{-}OCH_3$) to **1**($4\text{-}CO_2Et$) lay in the $\Delta S^{\ddagger}$ term, while $\Delta H^{\ddagger}$ remained fairly constant, or actually decreased. We suggested that a conformational change preceding the decomposition was responsible for this behavior. The tetrazenes **1** are expected to have conformation **2**, allowing conjugation of the amino nitrogens with the aryl rings. If decomposition were simply to involve stretching the N–N bonds, no benzylic stabilization of

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[1] A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, p 5 and throughout.

[2] R. I. Walter, *J. Amer. Chem. Soc.*, **88**, 1923 (1966).

[3] For a review of Hammett behavior of esr splittings, see E. G. Janzen, *Accounts Chem. Res.*, **2**, 279 (1969).

[4] J. Sinclair and D. Kivelson, *J. Amer. Chem. Soc.*, 90, 5074 (1968).

[5] B. M. Latta and R. W. Taft, *ibid.*, **89**, 5172 (1967).

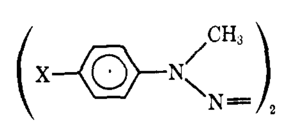
[6] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, p 327.

[7] For a review see ref 1, p 111.

[8] F. A. Neugebauer and P. H. H. Fischer, *Chem. Ber.*, **98**, 844 (1965).

[9] F. A. Neugebauer and S. Bamberger, *Angew. Chem., Int. Ed. Engl.*, 10, 71 (1971).

[10] S. F. Nelsen and D. H. Heath, *J. Amer. Chem. Soc.*, **91**, 6452 (1969).



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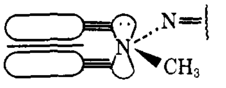

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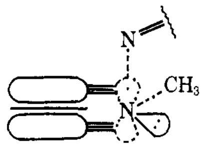

3

the incipient arylamino radical could occur, because the breaking bond would be perpendicular to the π system. For maximum stabilization of the forming radicals, the transition state should approach **3**, in which the nitrogen lone pair has been deconjugated from the aryl π system. Similar considerations would apply to hydrazine decompositions, which would rule out observations like Wieland's on compound stability as being directly related to odd-electron delocalization.

In this paper, we wish to report further support for the necessity of a conformational change to conjugate the lone pair from the aromatic system preceding 2-tetrazene decomposition and also an esr study of *N*-*tert*-butylanilino radicals which shows that they belong in Walter's "class S" on the criterion of spin density at nitrogen.

Results and Discussion

If the rate dependence upon substituent for **1** is really to belong to the conformational change of **2** to **3** preceding decomposition, a compound forced sterically out of conformation **2** must decompose with greater ease. To see if this would really be the case, we prepared tetrazene **4**, which differs from **1**(4-CO_2ET), the slowest decomposing compound for which we were able to measure a rate,[10] only by the presence of the 2-methyl groups. The hoped-for change in conformation to largely deconjugate the amino nitrogen lone pair from the aryl group was obvious from the uv spectrum of **4**, which had its longest wavelength λ_m at 345 nm, compared with 377 nm for **1**(4-CO_2ET), and 347 nm for **1**(4-H). The decomposition rate was measured by nitrogen evolution over a 40° temperature range, as summarized in Table I. Least-squares activation parameters determined from this data were $\Delta H^\ddagger$ = 28.4 kcal/mol and $\Delta S^\ddagger$ = 3.2 eu. The relative rates of decomposition of **4**, **1**(4-OCH_3), and **1**(4-CO_2ET) were 1 : 0.71 : 0.003. The 2-methyl substituents completely eliminated the rate-slowing effect of the 4-CO_2ET group, as expected for the conformational change argument; this effect on decomposition rate is completely unexplainable on the basis of stability of the radicals formed. Since the original goal of this research was to determine the substituent effect upon electronic delocalization in anilino radicals, we next turned to esr studies as a means of accomplishing this goal. Since the nitrogen splitting is directly proportional to spin density directly at the nitrogen nucleus, any increase in spin density in an s-hybridized orbital would lead to an even greater nitrogen splitting (a(N)) than a similar increment in p-orbital spin density. This makes a(N) a particularly sensitive tool for observing a preferential lone-pair *vs.* odd-electron delocalization. The *N*-methylanilino radical precursors already in hand were not convenient to use for these esr studies, both because of the large $a(N-CH_3)$ splitting expected, and because the β hydrogens would be easily abstracted, leading to inconveniently short radical lifetimes. We therefore prepared a series of 1,4-diaryl-1,4-di-*tert*-butyl-2-tetrazenes (**8**) by the obvious route shown in eq 1.

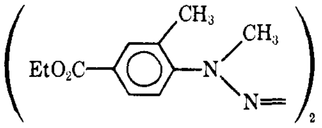

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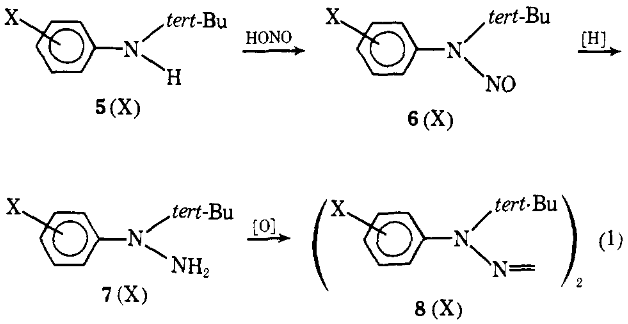
Table I. Decomposition Rate of **4** in Cumene

Temp, °C	10^4k, sec^{-1}
110.2	21.0
99.27	7.72, 8.12
90.38	3.21, 3.37
79.56	0.86, 0.95
69.82	0.24, 0.26



5(X)

6(X)

7(X)

8(X)

(1)

The *N*-*tert*-butylanilines **5** were prepared by alkylation of the anilines with *tert*-butyl iodide.[11] Because of the low reactivity of the less basic anilines, it was found desirable to modify Hickenbottom's procedure by the use of a low-polarity solvent (benzene–carbon tetrachloride) and long reaction times; in this way high degrees of tertiary butylation could be accomplished. We prepared the 4-cyano compound by reaction of **5**(4-Br) with cuprous cyanide in DMF.[12] Zinc–acetic acid reductions were used for all but **7**(4-OCH_3) (for which $LiAlH_4$ was far superior), but this step always gave fair amounts of cleavage back to **5**. Fortunately, the presence of **5** did not interfere with the oxidation of **7** to **8**, which was accomplished in good yield with benzoquinone as the oxidant.

At this time we have only determined nitrogen evolution rates for **8**(4-OCH_3) and **8**(4-H); the results are summarized in Table II and show a large amount of scatter. The observed rate ratio of **8**(4-OCH_3):**8**(4-H) was 5.5 (at 81°), to be compared with the previously determined[10] **1**(4-OCH_3):**1**(4-H) ratio of 24 (at 110°). This is consistent with the larger size of the *N*-alkyl substituent of **8** twisting it substantially out of conformation **2**.

It was of particular importance to prove that the esr spectra observed upon decomposition of the tetrazenes **8** were actually caused by the *N*-*tert*-butylamino radicals

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(11) W. J. Hickenbottom, *J. Chem. Soc.*, 946 (1933).

(12) L. Friedman and K. Shechter, *J. Org. Chem.*, **26**, 4684 (1961).

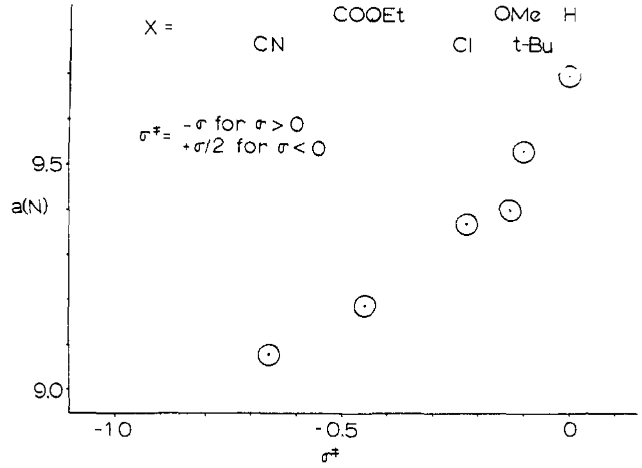
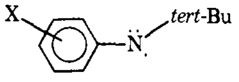
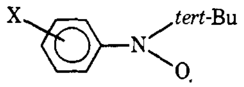


Figure 1. Correlation of a(N) for *N*-*tert*-butylanilino radicals (**9**) with $\sigma^{\ddagger}$.

9 and not by the related nitroxides **10**, which would give qualitatively similar spectra. The mis-identification of nitroxide for amino radical has occurred twice for the diphenylamino case.[13] We found that the nitroxides **10** could be observed easily in poorly degassed samples. These nitroxides had g factors of 2.0059 ± 0.0002 in hydrocarbon solvents, as expected, but somewhat different splitting constants (Table III) from the literature values,[14] which were determined in ethylene glycol; nitroxide splittings are well known to be rather highly solvent dependent. The splittings of the nitroxides **10** were also noticeably temperature dependent. We did a brief study of **10**(4-H) in isopentane and observed the nitrogen splitting to increase from 10.90 G at −130° to 12.10 at +20°, while the ortho splitting (which was not resolved from the para splitting in these experiments) decreased from 2.30 at −130° to 2.05 at −30°; the meta splitting remained about constant at 0.91 ± 0.02.


9 (X)


10 (X)

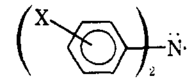

11 (X)

Table II. Decomposition Rates in Cumene

8(4-H)		8(4-OCH$_3$)	
Temp, °C	10^4k, sec^{-1}	Temp, °C	10^4k, sec^{-1}
81.0	0.46, 0.50, 0.51	65.9	0.26, 0.30
89.4	1.11, 1.23, 1.25	74.1	1.34, 1.56
97.4	3.34, 3.79, 3.84	81.0	2.31, 2.68, 3.13
105.3	7.11, 7.81	88.1	3.79, 4.69, 5.14
111.8	10.2, 10.9, 11.5	96.8	14.2, 14.7, 14.9
117.7	15.1, 15.7, 17.7		

Table III. Esr Splitting Constants for Aryl *tert*-Butyl Nitroxides in *n*-Heptane

Compd	Temp, °C	a(N)	a(H$_o$)	a(H$_m$)	a(other)
10(4-H)	−60	11.86	2.16	0.92	2.21 (1 H)
10(4-Br)	−60	11.61	2.30	0.90	
10(4-CO$_2$Et)	0	10.97	2.26	0.97	
10(4-CN)	−60	10.06	2.46	0.94	0.41 (1 N)

We chose *n*-alkanes as the solvents which would interact least with the amino radicals **9** and give the most reliable information on spin density in the unperturbed radical. We were successful in observing the arylamino radical **9** in fully degassed solutions upon photolysis of 4-OCH$_3$-, *tert*-Bu-, H-, Cl-, CO$_2$Et-, and CN-substituted **8**.[15] These radicals gave g factors in the range 2.0035 ± 0.0002, as expected for **9**, and substantially different splittings from the nitroxide radicals. No temperature dependence of the splitting constants (to a ±0.05-G accuracy) was observed over a greater than 100° range, so the splittings are quoted in Table IV[16,17] without the temperature at which the spectrum was recorded. Large amounts of line broadening were observed at low temperatures with **9**(4-OCH$_3$) apparently because of slowed rotation of the methoxyl substituent, but we were unsuccessful at reaching the low-temperature limit. The data in Table IV show that *N*-*tert*-butylamino radicals **9** belong in Walter's class S on the basis of the nitrogen splitting (and as discussed in the introductory section, no other radicals are known to be in this class on the basis of their esr spectra). Following Dewar,[18] who pointed out that electron donor substituents ought to be about twice as good at stabilizing a positive charge as an odd electron, Walter has suggested that for a class S radical, the effect of substitution should be approximately proportional to $\sigma/2$ for $\sigma < 0$, and to $-\sigma$ for $\sigma > 0$. The result of such a correlation on **9** is shown in Figure 1. A rea-

Table IV. Esr Splitting Constants for *N*-*tert*-Butylanilino Radicals, Diarylamino Radicals,[16] and Dialkylamino Radicals[17]

Compd	a(N)	a(H$_o$)	a(H$_m$)	a(other)
9(4-OCH$_3$)	9.40	5.61 (2 H	1.97 (2 H	0.91 (3 H)
9(4-*tert*-Bu)	9.53	5.74	1.86	
9(4-H)	9.70	5.84	1.99	7.09 (1 H)
9(4-Cl)	9.37	5.86	1.89	0.91 (1 Cl)
9(4-CO$_2$Et)	9.19	5.74	2.07	0.40 (2 H)
9(4-CN)	9.08	5.77	2.11	1.01 (1 N)
11(4-OCH$_3$)	8.49	3.47 (4 H)	1.18 (4 H)	0.59 (6 H)
11(4-*tert*-Bu)	8.7	3.7	1.5	
11(4-H)	8.9	3.70	1.49	4.34 (2 H)
Me$_2$N·	14.78			27.36 (6 H)

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[13] Reference 1, p 113.

[14] H. Lemaire, Y. Marechal, R. Ramasseul, and A. Rassat, *Bull. Soc. Chim. Fr.*, 2378 (1969).

[15] We were completely unable to obtain esr spectra of **9**(4-Br) by photolysis of the tetrazene, presumably because of the lability of the bromine substituent. In an attempt to increase solubility of the tetrazene by using THF, we observed a five-line spectrum which is apparently the radical cation of the tetrazene.

[16] (a) F. A. Neugebauer and P. H. H. Fischer, *Chem. Ber.*, **98**, 844 (1965); (b) F. A. Neugebauer and S. Bamberger, *Angew. Chem., Int. Ed. Engl.*, 10, 71 (1971).

[17] W. C. Danen and T. T. Kensler, *J. Amer. Chem. Soc.*, **92**, 5235 (1970).

[18] M. J. S. Dewar, *ibid.*, 74, 3353 (1952).

Table V. Nmr Chemical Shifts[a] and Yields for **8** and Precursors

Compd(4-X)	d, J = 8–9	d, J = 8–9	*tert*-Bu(s)	NH(s)	Mp or bp (mm), °C	Yield, %
5 (OCH_3)	3.28 (s)		8.82	7.00	85 (10)	22[b]
5 (*tert*-Bu)	2.87	3.53	8.87, 8.44	6.90	87–89 (0.8)	16[b]
5 (H)	2.67–3.46 (m)		8.73	6.67	70–75 (2)	16[b]
5 (Cl)	2.93	3.40	8.72	6.69	62–67 (0.2)	17[b]
5 (Br)	2.85	3.59	8.70	6.60	84 (2)	60[c]
5 (CO_2Et)	2.15	3.42	8.67	5.88	139 (0.45)	75[c]
5 (CN)	2.64	3.17	8.61	6.00	103–105	95[d]
6 (OCH_3)	3.11 (m)		8.43		50–52	73
6 (*tert*-Bu)	2.47	3.15	8.40, 8.65		103--104	55
6 (H)	2.43–3.20 (m)		8.40		60–62	85
6 (Cl)	2.67	3.20	8.43		96–98	73
6 (Br)	2.47	3.31	8.42		118–119.5	74
6 (CO_2Et)	1.96	3.14	8.42		90–91	59
6 (CN)	2.25	2.95	8.43		142–143	65
7 (OCH_3)	2.89	3.22	8.73	6.57	108 (0.35)	44[e]
7 (*tert*-Bu)	2.55–3.55 (m)		8.70, 8.89	6.63	74–75	34
7 (H)	2.58–3.47 m)		8.88	6.49	47–48 (0.3)	50[e]
7 (Cl)	2.89 (m)		8.87	6.54	*f*	55[e]
7 (Br)	2.63	2.93	8.50	6.51	*f*	60[e]
7 (CO_2Et)	2.02	2.75	8.76	6.03	*f*	60[e]
7 (CN)	2.47	3.36	8.76	6500	*f*	40[e]
8 (OCH_3)	3.01–3.17		9.00		128–129 dec	32
8 (*tert*-Bu)	3.09	2.70	8.79, 8.93		142–143 dec	72
8 (H)	2.52–3.13		8.97		30–131 dec	60
8 (Cl)	2.54	2.91	8.92		131–132 dec	82
8 (Br)	2.61	3.15	8.96		144–145 dec	80
8 (CO_2Et)	1.99	2.94	8.94		143–143.5 dec	80
8 (CN)	2.80	3.12	9.06		150–151 dec	60

[a] In τ, CCl_4 or $CDCl_3$ solvent. [b] Hickenbottom's conditions.[11] [c] Conditions as for **5**(Br). [d] See Experimental Section for conditions. [e] Yield estimated by nmr for mixture with amine. [f] Pure sample never obtained.

sonably smooth concave curve is observed for the $\sigma > 0$ substituents, corresponding to more positive σ substituents causing less of a decrease in a(N) than would be expected from the splitting observed for less positive σ substituents.[19] This could be interpreted in terms of the lone-pair–odd-electron competition discussed above, with lone-pair delocalization starting to become relatively more important with higher σ substituents; and such an effect clearly never becomes important enough to cause class O behavior.

Danen and Kensler[17] report INDO calculations which gave spin densities of 0.85 (N 2p) and 0.039 (N 2s) for the dimethylamino radical. Combined with their observed a(N) value, this corresponds to an effective Q(N) of about 16.6. The diphenylamino radical has a nitrogen splitting of 8.9 G, yet at least 60% of the spin density is in the aryl groups, according to Neugebauer and Bamberger.[16b] This means that the effective Q(N) must be above 22.5 (a value of 28 was used[16b] to fit the experimental data to McLachlan calculations). Comparing the splittings of *N-tert*-butylamino (**9**) and diphenylamino (**11**) radicals, the most striking feature is the similarity in size of the nitrogen splittings. Considering splitting ratios of **9**/**11** for the three examples in which identical substituents have been run, the ortho and para a(H) ratios fall in the range 1.54 to 1.63, yet the a(N) ratios are 1.09 to 1.11. Although it could be argued that cancellation effects could be concealing a fair amount of spin actually present in the *N-tert*-butyl group, we saw peak-to-peak line widths of about 0.25 G, so the *tert*-butyl splitting was quite small. Since there are two aromatic rings in **11**, but only one in **9**, the nitrogen spin density for **9** appears to be about 25% greater than that of **11**. This leads to an effective Q(N) for **9** as being intermediate between those of dialkyl- and diarylamino radicals. The reason for the appreciable increase in Q(N) as alkyl substituents are changed to aryl ones is not apparent to us, but must be taken into account if nitrogen splittings are to be translated into spin densities at nitrogen. Danen and Kensler[20] have demonstrated that Q(N) is not appreciably sensitive to closing the C–N–C bond angle in dialkylamino radicals, and all the amino radicals investigated to date appear to have very predominantly p hybridization in the odd-electron orbital.[21]

Experimental Section

1,4-Bis(4-carbomethoxy-2-methylphenyl)-1,4-dimethyl-2-tetrazene (**4**) was prepared from commercial 2-methyl-4-nitrobenzoic acid by esterification (H_2SO_4–EtOH), catalytic hydrogenation to the 4-amino ester (Pd/C, H_2), N-methylation (dimethyl sulfate–2 *M* sodium hydroxide), N-nitrosation (aqueous sodium nitrite), reduction to the hydrazine (zinc–acetic acid), and oxidation to the tetrazene (lead dioxide in benzene), using procedures previously described.[10] The tetrazene[22] decomposed at 106–108° (gas evolution); nmr ($CDCl_3$) τ 2.05 (br s, H_3), 2.10 (d of m, H_5), 2.85 (d of m, H_6), 5.80 (q, OCH_2), 6.71 (s, NCH_3), 7.55 (s, CCH_3), 8.62 (t, CH_2CH_3); uv (DME) λ_m 345 nm (ϵ 2.9×10^4), 232 (1.9×10^4).

1,4-Diaryl-1,4-di-*tert*-butyl-2-tetrazenes (**8**). Since all of the tetrazenes **8** were prepared by similar methods, detailed experimental data for the 4-bromo series will suffice. Experimental data are summarized in Table V.[22]

***N-tert*-Butyl-4-bromoaniline** (**5**(4-Br)). *tert*-Butyl iodide (42 g, 0.228 mol) was added to a mixture of 35 g (0.204 mol) of *p*-bromoaniline in 100 ml of benzene and 100 ml of carbon tetrachloride, and stirred for 10 days at ambient temperature. The residue after solvent removal was suspended in ether and extracted with 150 ml

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(19) Janzen[2] should be consulted for arguments and experimental facts showing linear correlation of a(N) and σ for class O radicals. The curvature in Figure 1 would be even greater if σ^- were used.

(20) W. C. Danen and T. T. Kensler, *Tetrahedron Lett.*, 2247 (1971).

(21) We thank Professors Danen and Neugebauer for helpful discussion.

(22) Adequate combustion analyses were obtained for the tetrazenes used in this work.

of saturated sodium carbonate, giving a 44:56 mixture of **5**(4-Br) : *p*-bromoaniline. Two repetitions of the procedure gave after distillation a 60% overall yield of **5**(4-Br) as a 9 : 1 mixture with starting material.

N-*tert*-**Butyl-*N*-nitroso-4-bromoaniline (6(4-Br)).** A solution of 9.1 g of sodium nitrate in 32 ml of water was added to 10 g of 90% *tert*-butylated aniline (**5**(4-Br), 0.039 mol) suspended in 18 ml of concentrated hydrochloric acid and 50 g of ice. The mixture was stirred for 2 hr in an ice bath, filtered, and crystallized from ethanol, giving 6(4-Br); ir, no NH; satisfactory analyses were obtained for $C_{10}H_{13}BrNO$.

N-*tert*-**Butyl-*N*-4-bromophenylhydrazine (7(4-Br)).** 6(4-Br) (4 g, 0.155 mol) in 7 ml of acetic acid was added to 21 g of activated[23] zinc dust in 7 ml of water, keeping the mixture under 10°. After stirring 2 hr, the mixture was filtered, the cake washed with three 10-ml portions of 5% hydrochloric acid, and the filtrate basicified with 100 ml of 20% sodium hydroxide and extracted with five 10-ml portions of ether. The residue after solvent removal consisted of 3.2 g of a 60 : 40 mixture of hydrazine and amine.

1,4-Di-*tert*-butyl-1,4-bis(4-bromophenyl)-2-tetrazene (8(4-Br)). To 3.2 g of the above hydrazine-amine mixture (*ca.* 7.5 mmol) in 60 ml of absolute ethanol was added 0.95 g (8.8 mmol) of thrice-sublimed quinone in ethanol at −10°. The mixture was stirred for 2 hr at −10°, the ethanol was vacuum distilled out of the cold reaction mixture, and the residue was washed with ethanol, cooled to −78° until white, and crystallized from ethanol.

N-*tert*-**Butyl-*p*-cyanoaniline (5(4-CN)).** A mixture of 25 g (0.11 mol) of **5**(4-Br) in 150 ml of dimethylformamide and 16 g (0.18 mol) of cuprous bromide was refluxed 36 hr, cooled, and poured into 200 g of sodium cyanide in 600 ml of water. The organic layer was separated and the aqueous solution extracted with 250 ml of benzene. The combined organic layers were washed with 200 ml of sodium cyanide and dried over sodium sulfate, the solvent was removed, and the residue was crystallized from water.

Esr spectra were recorded on Varian E-3 or E-15 equipment, the splittings and *g*-factors calibrated with Fremy's salt. Samples in 3-mm quartz tubes were irradiated with a 2.5-kW Hanovia mercury-xenon lamp filtered by 15 cm of a cobalt-nickel salt mixture, or with a Bausch and Lomb high intensity monochromator and an Osram SP-200 lamp.

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Thermodynamic Stabilities of Some Cyclic Halonium Ions in Magic Acid[1]

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Abstract: The heats of formation of a series of methyl-substituted ethylene- and tetramethylenebromonium ions and a chloronium ion from the appropriate dihaloalkane precursors were measured calorimetrically in 11.5 mol % SbF_5–FSO_3H solution at −60°. The tetramethylenebromonium ions are about as stable as the *tert*-butyl cation and are *ca.* 10 kcal/mol more stable than a correspondingly substituted ethylenebromonium ion. The tetramethylenechloronium ion is *ca.* 7.5 kcal/mol less stable than its bromo analog. The interaction of a methyl group with a three-membered ring seems to be unusually favorable.

One of the most thoroughly studied families of organic intermediates is the cyclic halonium ions. However, there has been no information available on their thermodynamic stability. Accordingly, we have measured calorimetrically the heats of formation of a series of halonium ions from dihalide precursors in 11.5 mol % SbF_5–FSO_3H solution at −60°.

Several lines of evidence point to the existence of halonium ions as intermediates in a variety of reactions. The evidence for bromonium ions as intermediates in the addition of bromine to olefins is substantial and generally accepted.[2] Winstein developed a convincing case for the intermediacy of cyclic three-membered bromonium and iodonium ions through a detailed analysis of the solvolysis rates of *trans*-2-halocyclohexyl brosylates.[3] No evidence for chloronium ions was found.[4] Peterson has demonstrated the intermediacy of five-membered ring halonium ions in the addition of trifluoroacetic acid to 5-haloolefins.[5–10] In this work, good evidence for the chloronium ion as well as the bromonium and iodonium ions was obtained. Later work by both Peterson and Trahanovsky gave evidence for the same intermediates in solvolysis reactions.[11–13] In addition to their observation as unstable intermediates, stable halonium ion salts have been isolated.

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